VALENTIN'S
PRACTICAL CHEMISTRY

BY

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TENTH EDITION

PREFACE TO THE TENTH EDITION.

In this edition easy experimental work has been introduced in the early chapters on the composition of air and water, diffusion, some carbon compounds, sulphur and sulphuric acid, followed by exercises on quantitative analysis, volumetric analysis, methods of ascertaining molecular weight, &c.

The "Experiments" on metals and non-metals comprised under "Reactions of the Metals" &c., have been thoroughly revised and extended, and the microscopic structure of some common alloys illustrated by photographs.

Appendix I. ("Rare Metals") has been brought up to date.

It is suggested to the teacher that students after performing or seeing some of the experiments in the early chapters should be assisted with some typical examples in Chapter VI, ("Quantitative Exercises"), and these followed by fractional distillation, determination of melting-point, molecular weight, and examples from the volumetric analysis section.

Particular attention should be given by the student to the experiments and reactions detailed under each metal of the analytical groups.

For advice and assistance in the earlier chapters and the "Rare Metals" I am indebted to Dr. F. E. Matthews and Mr. J. S. S. Brame, F.C.S., respectively. The micrographs of alloys are by Mr. A. H. Coote, B.Sc.

W. R. HODGKINSON.

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INTERNATIONAL ATOMIC WEIGHTS—1906.

		O = 16.				O = 16.
Aluminium	Al	27·1	Neodymium	.	Nd	143·6
Antimony	Sb	120·2	Neon	.	Ne	20
Argon	A	39·9	Nickel	.	Ni	58·7
Arsenic	As	75·0	Nitrogen	.	N	14·04
Barium	Ba	137·4	Osmium	.	Os	191
Bismuth	Bi	208·5	Oxygen	.	O	16·00
Boron	B	11	Palladium	.	Pd	106·5
Bromine	Br	79·96	Phosphorus	.	P	31·0
Cadmium	Cd	112·4	Platinum	.	Pt	194·8
Cæsium	Cs	132·9	Potassium	.	K	39·15
Calcium	Ca	40·1	Praseodymium	.	Pr	140·5
Carbon	C	12·00	Radium	.	Rd	225
Cerium	Ce	140·25	Rhodium	.	Rh	103·0
Chlorine	Cl	35·45	Rubidium	.	Rb	85·5
Chromium	Cr	52·1	Ruthenium	.	Ru	101·7
Cobalt	Co	59·0	Samarium	.	Sm	150·3
Columbium	Cb	94	Scandium	.	Sc	44·1
Copper	Cu	63·6	Selenium	.	Se	79·2
Erbium	Er	166	Silicon	.	Si	28·4
Fluorine	F	19	Silver	.	Ag	107·93
Gadolinium	Gd	156	Sodium	.	Na	23·05
Gallium	Ga	70	Strontium	.	Sr	87·6
Germanium	Ge	72·5	Sulphur	.	S	32·06
Glucinum	Gl	9·1	Tantalum	.	Ta	183
Gold	Au	197·2	Tellurium	.	Te	127·6
Helium	He	4	Terbium	.	Tb	160
Hydrogen	H	1·008	Thallium	.	Tl	204·1
Indium	In	115	Thorium	.	Th	232·5
Iodine	I	126·97	Thulium	.	Tm	171
Iridium	Ir	193·0	Tin	.	Sn	119·0
Iron	Fe	55·9	Titanium	.	Ti	48·1
Krypton	Kr	81·8	Tungsten	.	W	184
Lanthanum	La	138·9	Uranium	.	U	238·5
Lead	Pb	206·9	Vanadium	.	V	51·2
Lithium	Li	7·03	Xenon	.	Xe	128
Magnesium	Mg	24·36	Ytterbium	.	Yb	173·0
Manganese	Mn	55·0	Yttrium	.	Yt	89·0
Mercury	Hg	200·0	Zinc	.	Zn	65·4
Molybdenum	Mo	96·0	Zirconium	.	Zr	90·6

NEWLANDS'S AND MENDELEEFF'S TABLE OF THE ELEMENTS ARRANGED AS A PERIODIC SERIES

Series.	Group I. R_2O.	Group II. RO.	Group III. R_2O_3.	Group IV. RH_4 RO_2.	Group V. RH_3 R_2O_5.	Group VI. RH_2 RO_3.	Group VII. RH R_2O_7.	Group VIII. RO_4.
1	$H=1$							
2	$Li=7$	$Be=9·0$	$B=11$	$C=12$	$N=14$	$O=16$	$F=19$	
3	$Na=23$	$Mg=24$	$Al=27$	$Si=28$	$P=31$	$S=32$	$Cl=35·5$	
4	$K=39$	$Ca=40$	$Sc=44$	$Ti=50$	$V=51$	$Cr=52$	$Mn=55$	$Fe=56, Co=59$ $Ni=58, Cu=63$
5	$(Cu=63)$	$Zn=65$	$Ga=69$	$Ge=72$	$As=75$	$Se=79$	$Br=80$	
6	$Rb=85$	$Sr=87$	$Yt=89$	$Zr=90$	$Nb=94$	$Mo=96$	$—=100$	$Ru=104, Rh=104$ $Pd=106, Ag=108$
7	$(Ag=108)$	$Cd=112$	$In=113$	$Sn=118$	$Sb=122$	$Te=125$	$I=127$	
8	$Cs=133$	$Ba=137$	$La=138$	$Ce=140$	—	$Di=145$		
9	$(—)$	—	—					
10	$—165$	169	$Er=170$	$Yb=172·6$	$Ta=182$	$W=184$		
11	$(Au=196)$	$Hg=200$	$Tl=204$	$Pb=206$	$Bi=210$	—	—	$Pt=194, Os=195(?)$ $Ir=192, Au=196$
12	—	—	—	$Th=231$	—	$U=238$	—	—

CROOKES' LEMNISCATE DIAGRAM OF SYNTHESIS OF ELEMENTS.

(See Crookes' presidential address, Chemical Society, 1888.)
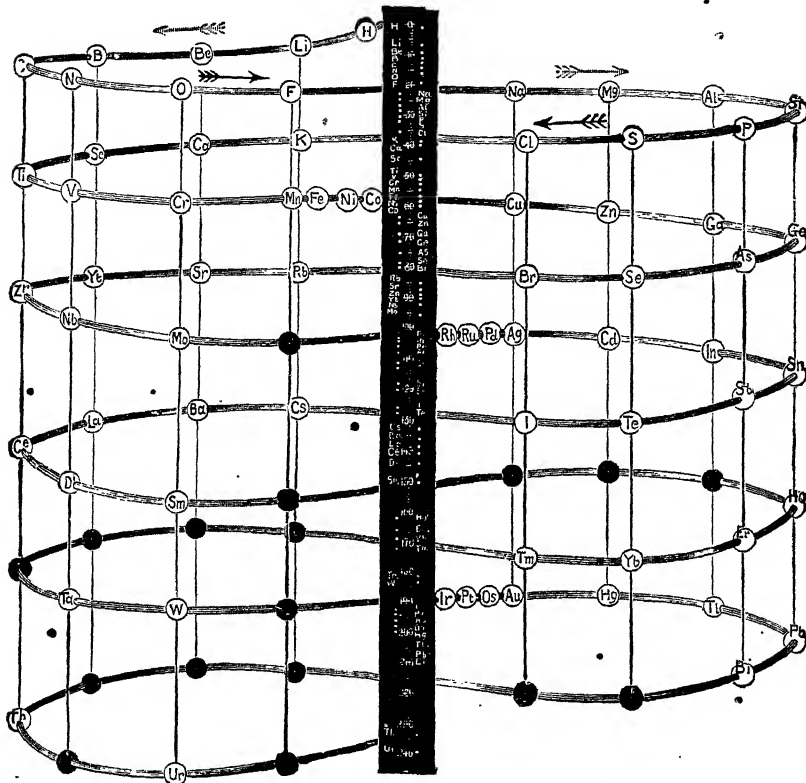
This and the previous diagram exhibit the genetic relations of the elements to each other as derived from their atomic weights and general chemical characters.

Both attempt to show the periodic recurrence of similar functions or properties, and the probable existence of " triads " or groups of several elements whose properties and general behaviour are very similar.

A COURSE

OF

PRACTICAL CHEMISTRY.

INTRODUCTION.

PRACTICAL or experimental chemistry may be analytical—that is, simplifying or taking apart—or synthetical.

Analysis may be by weight or volume, and is then "quantitative," or may be simply the performance of reactions or tests to ascertain the quality or nature of a substance, or "qualitative."

Synthesis is the making or building up of a compound—of either mineral or organic nature—by starting from some elements or comparatively simple compounds, and, following some particular line of procedure, uniting them so as to form a definite new substance.

Many synthetic methods have been indicated more or less distinctly by the results of analytic ones, or are based on theories originating from a consideration of analytical results.

All forms of matter possess certain definite properties, and it is upon some variation in one or more of these properties that we have to depend for the identification of different forms of matter. The properties of matter fall easily into two groups: (1) physical, (2) chemical.

The physical properties of matter deal with matter in a state of apparent repose, and some of them, as colour, hardness, relative weight, &c., are at once noticeable.

The chemical properties of a substance are not evident on sight. They are ascertained only by studying its behaviour with or towards other substances when brought into intimate contact therewith under some particular physical conditions, such as the temperature, degree of electrical excitation, &c.

Physical forces may alter a substance for the time being, the substance reverting to its original form or state after the force has ceased to act. With a chemical action the change is, as

surface. If made hot enough the silver may melt, but be as good-looking as ever. If they were weighed beforehand, the iron, with the dirt produced on it, will be found to be heavier after the heating than before, and the silver will not have changed.

If this simple operation of heating be conducted in a vessel from which the air has been removed by a pump no change in appearance or weight will in either case take place. This indicates the surrounding air, or some part of it, as being the probable cause of the change.

Experiment and observation have proved that it certainly is one of the constituents of the air with which we have to deal in many cases of change of this type, and in many experiments and operations carried on under ordinary circumstances—that is, in contact with air.

The atmosphere consists of a mixture of several gaseous substances, one of which in particular is active in attacking—which is the same thing as combining with—many other substances. It is taking part in many operations we perform in ordinary air, and is, in fact, one of the first, if not the foremost, material from which the definite idea of chemical action or combination has been obtained.

The air has been found to consist mainly of about 20 per cent. of this active constituent, called oxygen; about 78 per cent. of nitrogen, a much less active substance; a small quantity of some other gases, also of a supposed elementary or simple nature, named argon, helium, neon, &c., amounting in the aggregate to about 1 per cent., and about which little of a chemical nature is yet known; and a few other substances, of which carbon dioxide and water vapour are the most important.

The relative amounts of these substances vary a little from place to place and time to time. This is particularly the case with water vapour. With the exception of the water vapour, the composition of the atmosphere is, however, remarkably constant for a common " mixture," which it undoubtedly is.

ELEMENTS AND COMPOUNDS.—The materials dealt with in chemistry belong to one or the other of these classes. Some of the constituents of the air, just mentioned, are considered to be of a peculiar simple nature, which is expressed by the term " element."

Generally this term is applied to a substance—which may be a gas, liquid or solid—that suffers no permanent change in weight or other properties when submitted to the most severe physical treatment.

A feeble idea of this may be obtained from some experiments with sulphur (Fig. 1). Place a small quantity of sulphur in a flask or dry glass tube. Heat gently over a flame until it melts to a yellow limpid liquid. Stir with a thermometer until it begins to set (this should be about 115° C.). Now melt up again, without the thermometer; incline the tube or flask, and heat as strongly as possible until the sulphur boils and dark vapours pass over into the other tube. (The boiling temperature here is too high for an ordinary thermometer.)

A yellow deposit or a liquid may condense in the tube, and some of the vapour may catch fire and burn at the mouth of the boiling

tube or little flask. Collect some of the substance that has distilled over. Melt it gently, and stir with the thermometer as before. It will be found to behave precisely the same as before distilling. This test is by no means a severe one. It is not difficult to send powerful electric sparks through this vapour of sulphur whilst it is distilling, and the condensed sulphur will still be found to be unchanged in its properties. Sulphur can also be dissolved in a liquid, as oil of turpentine ("turps"), and obtained therefrom again, of the same melting-point, by letting the "turps" evaporate away.

The melting temperature, or "melting-point," is one of the most characteristic physical properties of a substance, and is frequently employed for identification or for proof of purity (see later).

Many substances of the class "compound" will also withstand the temperature necessary to melt, boil, or vaporise them, and some are known which resist the electric arc temperature or electric sparks passing through them. So that this alone is not a sufficient criterion of an element. Several conditions have to be satisfied before a substance can be with any certainty classed as "elementary," but the idea is that

FIG. 1.

nothing differing from itself, as it stands, can be extracted from it—or, in other words, it cannot be decomposed.

"Compounds" consist of two or more "elements"—not simply mixed anyhow, but *united* in such a peculiar manner that really a new material is formed.

As a practical example, make an intimate mixture of iron filings and powdered sulphur. Evidently the two may be mixed in any relative amounts. The colour of the mixture may be anything from yellowish to nearly black. If the mixture be "joggled" in a glass the iron filings will partly separate to the bottom. If put into water the filings will completely settle, and most of the sulphur will refuse to be wetted and will swim. A magnet stirred into the powder will attract and separate the iron. It is also possible to dissolve the sulphur and not the iron, or the iron and not the sulphur. But now place some of this mixture in a hard glass tube or a crucible, and heat strongly over a flame, watching the operation. The sulphur first will give off a little fume or smoke, and some will deposit on the top of the tube; it will melt, and then boil; and finally the iron will reach a certain temperature and begin to combine with the sulphur. It may even glow and become much hotter inside the tube or crucible than the flame can possibly make it from the outside. This is heat of chemical combination. The product may melt at the moment of formation owing to the development of this heat.

Some other metals, as copper, silver, tin, mercury, lead, show these effects quite as easily as iron with sulphur.
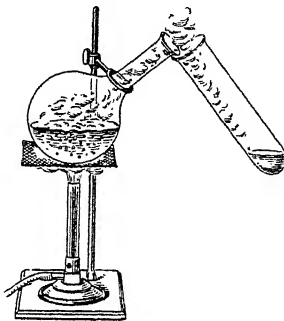
Now when this "chemical action" really takes place, it will be noticed that either some sulphur is driven off from the mixture and settles on the upper cool part of the tube, or that some iron filings are left. Generally the former will be the case.

On cooling, a product will be obtained which differs utterly in its appearance and properties from the metal or sulphur. The means of separation before mentioned, when it was a mixture, no longer apply. It *can* be dissolved, but now only as a whole, not as a metal *and* sulphur.

As will be seen, there is something of the nature of the "absolutely definite" in the character both of an element and a compound. The elements are possibly able to exist as such through any range of temperature. Many of the compounds we know and deal with practically exist only as such within a definite, and in some cases not very great, range of temperature. Within this range, however, a compound is an individual with as sharply marked and unchangeable properties as an element.

CHEMICAL ACTION.—Probably *the* primary condition for a chemical action to take place is real contact between the particles of the substances concerned. This contact is most easily and rapidly brought about between gases and least so with solids. Of the mechanism of a chemical action really very little is known. Elements join together, and apparently elements can attack compounds;* and one compound may attack another,† involving a redistribution of the elements of which each is composed.

The most important fact about a compound is that it may be formed by the combination of two or more elements in some way or other, but however any particular compound may be formed there is always the same amount by weight of each particular element contained therein, and no modification of the process of formation will alter the relative proportions of these constituents.

Chemical actions follow definite lines, and there is generally a selective action, as, for instance, when *a* can unite with *b* or *c*, but not with equal energy. Then a compound *ab* may be formed, and *c* come into play only when the quantity of *b* falls short of that requisite to make a compound.

In most cases of chemical union some energy, generally in the form of heat, is developed. It is a constant quantity. Where the tendency to unite is great the heat produced is generally more than where the tendency to union is less.

There are cases where no heat or energy of any kind is evolved at the time of formation of the compound.

* Place a very small quantity of corrosive sublimate (mercuric chloride) on a piece of clean copper, and moisten with a drop of water. On stirring with a match or quill it will be seen that the copper has become silvered on the surface and at the same time a greenish coloured substance formed.

† Place a very small piece of corrosive sublimate and a similar sized piece of potassium iodide in contact, or make a solution of each separately in a small volume of water and mix the solutions. The original compounds are white crystals; after redistribution the mass is coloured pink, because the mercury has changed over from the chlorine to the iodine.

In many of these cases the act of chemical union has to be assisted by the expenditure of energy in some form—heat or electric current—or by the use of indirect or roundabout processes, in each of which there is some consumption of energy.

These two classes of compounds are usually distinguished as *exothermic* (those in the formation of which energy as heat is produced) and *endothermic* (those compounds requiring an expenditure of energy in the shape of help from outside—*e.g.*, heating to some temperature the whole time the combination is taking place). They are purely relative terms, and mean that the members of one class have more potential energy at disposal than the others. The difference is most usually shown by the ease with which endothermic compounds can, as a rule, be made to perform some chemical action, or in many cases even decompose, when subjected to mechanical treatment like friction or percussion. Most, if not all, explosives belong to the endothermic class. Compounds of the exothermic class require the expenditure of energy to decompose them.

Chemical actions sometimes commence but slowly, or the materials may need to be heated to some essential starting temperature, and it may take some time before an action is completed. But in any case there is no such thing as "*nearly*"; *an action either does or does not take place*. It often happens, however, that after one action has commenced and reached a certain stage a second one starts, and the two appear to be going on together. This in some cases assumes a seesaw form, the primary product existing only for a short time, or a small amount only being formed as a "stage" of the reaction.

INTRODUCTION TO PRACTICAL CHEMISTRY.

Apparatus required.

The first essential is a reliable and reasonably sensitive balance, with a set of weights. A very simple balance will serve at first. The weights used are almost always metrical.*

Weights are usually supplied in boxes, and are arranged from 50 grms., thus: 50, 20, 10, 10, 5, 2, 1, 1, 1, and ·5, ·2, ·1, ·1, ·05, ·02, ·01, ·01, with some smaller which are seldom used. If the balance be wide enough the weights are most conveniently arranged on a piece of tile or white paper inside the case. They are then more easily accessible.

There should be also a rider, a small bent wire of weight ·01 grm., to be used on the beam itself. The beam is often graduated in

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* In the metrical system the metre is the practical unit of length. It is divided into tenths, hundredths, and thousandths. A cube of water the tenth of a metre long on each side and at a temperature of 4° C. constitutes the weight called a kilogram and the volume called a litre. The $\frac{1}{1000}$ of a kilogram is the gram, and the $\frac{1}{1000}$ of a litre is the cubic centimetre. This weight and this volume are so much used that they are commonly designated by the abbreviations grm. and c.c.

tenths and hundredths of its length, starting from the centre, to each end. The rider, when on the centre point of the beam, has no effect on either pan. When on the end mark it has the effect of ·01 grm. placed in the pan. At any intermediate position it will have some effect equivalent to the third or fourth decimal place.

When commencing to weigh, place first the substance on one pan; then commence by putting on the opposite pan the largest
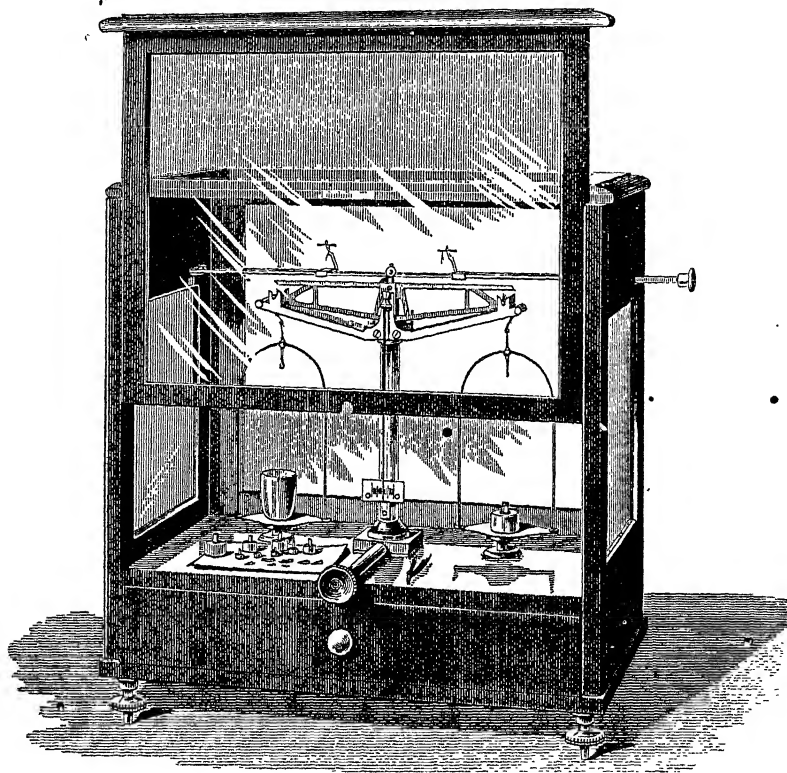
FIG. 2.

weight of the set. Slowly turn the handle, which generally relieves the balance-beam from its supports, and watch the direction of motion of the indicating needle on the scale in front. When it points in the direction of the pan on which are the weights, it indicates that more are required. Then add the next greater weight, bringing the balance to rest between each addition by turning up the beam supports. This must never be omitted. Never jump or guess at the weight, but always proceed in order from the greatest. As the correct weight is approached the balance will begin to swing slower. Do not wait until the beam comes to rest,

but proceed by the addition or taking away of weights until the needle swings nearly an even distance on each side of the centre mark of the scale. Let it swing three or four times. It will probably on first turning the beam loose swing to 6 on one side, and return past the centre to 8 or 10. If the beam is provided with a rider, now is the time to use it. Say the needle swings to 6 left, and recovers to 8 or 10 right, then more weight is wanted on the right side of beam. Place the rider on, this time beginning at the middle of beam, or the mark 5, and, again swinging, move the rider to less or more than 5, as the needle indicates. When it swings nearly evenly, turn up the beam to rest, and then carefully again liberate. It should be set swinging five or six degrees, and allowed to swing several times before arresting. If equilibrium has been obtained the swing will diminish regularly on each side of the centre. Bring to rest, and read off the values of the weights from the empty spaces, either in the weight-box or on the paper referred to as holding them in the balance-case. Pick the weights from the pan, and replace them in order, seeing at the same time that they tally with the weight recorded. It is advisable sometimes to reverse the positions of weights and substance. If the balance is in fair order the result should be practically the same.
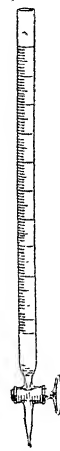
FIG. 3.   FIG. 4.
Pipette.   Burette.

One side or pan of the balance must be kept for the substance and the weights respectively. Nothing whatever must be placed on the naked pan, but always on a glass or porcelain or other vessel. This containing vessel must be, of course, itself weighed, either before or after, and its weight deducted from that of the substance.

Balances must be kept in one place and level on a steady bench. Nothing whatever should be put inside the balance case but the thing to be weighed and the weights. When weighing anything a book should be taken to the balance and the weighings entered at once.

A few measuring vessels, flasks, or cylinders and a burette are most useful. The graduated flasks should be 1 litre, $\frac{1}{2}$ litre, 250 c.c., and 100 c.c. The measuring cylinder should be 500 c.c., graduated into 1 c.c.

Burettes are generally made to hold a little more than 50 c.c., and there are 50 c.c. graduations, and each c.c. again into fifths or tenths. It is more convenient to have 55 or 60 c.c. divisions and each into fifths.

The burette and the gram weights should work together. The 50 c.c. of distilled water at 15° C. measured from the burette should be very close indeed to 50 grms. weight. Usually burettes are graduated with water at 15°–16° C.

Weighing should be practised first of all on the weights, the 50 grm. piece being tested against the collective small weights, then the 20 grm. against smaller pieces, and so on.

A small flask should then be weighed either by weights or counterpoised by shot, &c., 50 c.c. of distilled water introduced, and then weighed. This should also be done with 20 c.c. and 10 c.c. The result will not be exactly 50, 20, and 10 grms., but should not differ very widely therefrom. The weight of 1 c.c. water at 15° C.

FIG. 5.—Measuring Flask.   FIG. 6.—Measuring Cylinder.
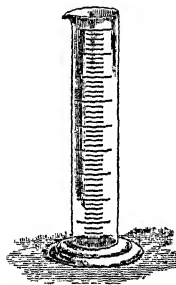
is not the same as that of 1 c.c. at 4° C., water expanding when warmed above the temperature of 4° C.

METALS AND NON-METALS.—In everyday life some substances of the " element " class are called "*metals,*" whilst this term is withheld from others.

Quite a number of elements have some characters in common. For instance, copper, silver, gold, iron, nickel, aluminium, are solids which can be moulded or shaped by pressure, polished or burnished by friction. They are more or less ductile—that is, can be drawn out or extended into wire; and they will withstand a considerable strain before breaking. They allow heat and electricity to flow along them with more or less ease. Some are very elastic and sonorous when struck. They do not dissolve as such, or unchanged, in any liquid.

A number of other substances, also elements, show few if any of these properties, or only to a very slight extent. They are termed " *non-metals.*" Some are gases, one is liquid at ordinary temperatures; and of the solids several are soluble—as sulphur and phosphorus, iodine, &c.—in liquids, and may be crystallised without chemical action or change from these solutions.

The line of demarcation is, however, *not a sharp one.* Some elements show the metallic property in an eminent degree, as gold, others nothing of it, as some gaseous elements, and others, again, are

somewhat intermediate in character. In addition there are some decidedly chemical differences, as will appear later. The terms metal and metallic and non-metal are useful if understood in a broad sense.

The practical employment to which a metal is applied depends partly on its physical and partly on its chemical properties.

Iron (and steel) heads the list in the matter of tensile strength and hardness, but it is somewhat easily acted upon by a number of other substances, which restricts its use or necessitates the employment of some protective.

Lead is one of the softest of the metals, and its tensile strength is very slight. It can, however, be easily rolled or pressed into sheets or tubes, and is not very rapidly acted upon chemically by things in ordinary use. Most of the common metals fall between iron and lead in the matter of hardness and softness, tensile strength, &c., although not in the matter of chemical resistance. Some are more resistant than lead, and others less so than iron.

Speaking broadly, metals show a greater tendency to unite with non-metals than with metals. Still, metals do unite, and these combinations are generally called "alloys." Sometimes the tendency to combine is slight, and then something like mixtures or solid solutions are obtainable. Some alloys seem to be of relatively simple composition, as brass, which may be considered as $ZnCu_2$, about 67 per cent. Cu and 33 Zn (this is not the universal opinion); or very complex, as steels undoubtedly are, consisting of a compound, as Fe_3C, combined with a considerable number of atoms of iron, perhaps after the manner in which water of crystallisation is held by some salts (see later, water of crystallisation in salts, " Iron," &c.).

CHAPTER I.

ON THE NATURE AND COMPOSITION OF ATMOSPHERIC AIR.

As stated (*ante*, Introduction), the air consists of a mixture of gaseous elements and compounds. The mixture has an exceedingly constant composition, owing mainly to the action of diffusion of gases. A litre (1000 c.c.) of dry air at 0° C. weighs 1·293 grm. Air may be dried by standing over or bubbling through concentrated sulphuric acid, or by contact with solid calcium chloride, these substances removing water only.

Dry air is appreciably heavier than damp or moist air, because water vapour is, bulk for bulk, much lighter than air, and, when present in air, is not dissolved, but exists side by side with the other gases, exerting part of the pressure of the whole. That is, supposing some ordinary air is exerting a pressure of 30 inches of mercury, and the water vapour can by some means be extracted from it, the pressure would be reduced.

The volume of this water vapour in air at any place can be ascertained by means of the apparatus shown in Fig. 7.

The flask, which may be of about 1000 c.c. capacity, has a gauge arranged to the side tube, and through the cork a burette and another tube, with tap.

The bent tube or gauge should contain as indicating liquid some weak sulphuric acid. The burette is charged with concentrated sulphuric acid, and the small side tap is for adjusting the air pressure at starting.

FIG. 7.—Flask with gauge and burette.

To use.—The flask must be quite dry, and may be filled with the air of the place by simply leaving open for a short time. The cork, with its burette and air tap, is then introduced, the gauge made level by just opening the tap and closing again. Now a few drops of sulphuric acid are allowed to fall in. The liquid in the outer gauge tube will at first rise slightly, and then within a few minutes fall, thus indicating

that the pressure inside is less than the external. Water vapour is being absorbed by the strong acid. More acid is now let in to bring the gauge again level. After one or two additions the gauge will remain constant. All the water vapour has been absorbed, and in its place a certain number of cubic centimetres of acid have been run in. The total capacity of the flask must, of course, be known.

The number of cubic centimetres of acid run in to make the pressure the same as at commencement is evidently the volume of water vapour existing in the air and exerting part of the total air pressure. Supposing the flask have 1000 c.c. capacity, and 14 c.c. of acid are run in before the gauge is level, it indicates that 14 c.c. of water vapour were present in the original air.

The flask should stand in a place of a steady temperature, and, beyond opening the taps, must not be touched by the hand during the operation, as all gases expand very much even when slightly heated.

EXPANSION OF A GAS.—If a gas be heated from the temperature of melting ice to 273° C. the volume will be doubled provided the pressure on it be kept constant.

If a certain volume of a gas, enclosed in a vessel provided with a pressure-gauge, be similarly heated from the melting-point temperature of ice to 273° C. the pressure of the enclosed gas in the vessel will be 30 inches (or 760 mm.) above the outside pressure.

Supposing in this experiment the gas, instead of being heated, were cooled from the ice temperature (0° C.) still further, the pressure-gauge will show a regularly diminishing pressure as the temperature falls, until at a temperature of 273° C. below the temperature of melting ice the gauge would show a total absence of pressure. This effect would result with a *perfect* gas—that is, a substance that could exist *only* in the gaseous state. This low temperature has not been obtained. Most, if not all, the known gases become liquefied, or even solidified, before this low temperature is reached. The known gases are therefore in this sense not quite perfect.

The temperature of 273° C. below the melting-point of ice is known as "absolute" zero.

The "particles," or molecules, or atoms of a "perfect" gas would, at this temperature, be at rest. The weight would be the same, but there would be no pressure on the sides of the containing vessel. It could scarcely be a vacuum vessel, for a perfect gas could not liquefy nor solidify. Its particles would be in the vessel, but standing still. The particles or molecules of all known gases are undoubtedly in a state of motion, moving very rapidly in all directions. It is the impact of these many particles or molecules on the sides of the vessel that constitutes the pressure of the gas. When heated the motion is accelerated, and the number of impacts per second increased; when cooled, the rate is lowered, and the number of blows per second falls. The pressure exerted by a gas in a closed vessel increases regularly with rise and diminishes with fall in

temperature. At some temperature, which is a constant for each gaseous substance, liquefaction takes place, and at a lower temperature solidification, and at some point a little below this there is generally a most excellent vacuum in the vessel, providing, of course, that it was filled with the particular gas only at the commencement of the experiment. The idea of "absolute" zero ($-273°$ C.), $0°$ C. abs., is founded on what would probably be the behaviour of a perfect gas.

Based on the foregoing is the statement that gases expand $\frac{1}{273}$ of their volume at $0°$ C. for every degree they are heated above and contract $\frac{1}{273}$ for every degree they are cooled below this temperature.

DIFFUSION.—The property of diffusion is not confined to gaseous substances, but exhibited by them in an eminent degree. Some of the effects may be seen by the use of quite simple apparatus.

FIG. 8.   Two glass cylinders, or ordinary bottles with narrow necks, are each filled with a gas—say hydrogen or coal gas in one and carbon dioxide or sulphur dioxide in the other. Join them together by the cork and tube, so that the hydrogen (or coal gas) is above and the much heavier gas below. After standing for thirty or forty minutes they may be taken apart, and the lower one tried with a flame and the upper one inverted in a basin of weak sodium hydroxide solution or weak ammonia. The alkaline liquid will dissolve the carbon or sulphur dioxide, and the liquid will rise in the bottle, showing, roughly, how much of the heavier gas has diffused upwards into the lighter in the time. If the contents of the bottom cylinder inflame when a lighted taper is applied to the mouth of the cylinder, it proves a considerable diffusion of the lighter gas downwards. Another arrangement which shows, qualitatively, the rate of diffusion of hydrogen compared with air is to affix by a cork a small porous, or unglazed, earthenware cylinder (battery cylinder) at the end of a glass tube. The tube may be a metre or more long, and somewhat less than a centimetre in diameter. The open end of the tube should be dipped under water, and a beaker inverted
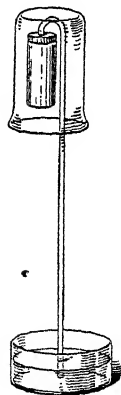
FIG. 9.   over the cylinder (see Fig. 9). Hydrogen or coal gas is blown into the beaker, and collects therein, being lighter than air. It begins at once to diffuse through the porous cylinder, driving air before it, as will be seen by the bubbles escaping from the immersed end of tube. Some air diffuses back into the lighter gas, but the advantage in rate is with the latter, and it acts against gravity. On removing the beaker of light gas after a few minutes water will be seen to rise in the tube somewhat rapidly and to a considerable height. After the light gas has entered the porous jar, and the beaker still contains the same gas, things assume a

steady condition—as much passes one way as the other through the walls of the porous jar. But when the outer beaker is removed light gas from the inside diffuses through into air quicker than air can diffuse back. There is therefore less pressure inside the glass tube and porous jar than outside, and the water rises to a certain height to equalise this difference.

The law as to diffusion is stated thus : Gases diffuse at rates inversely as the square roots of their relative densities. That is, for instance, hydrogen has only $\frac{1}{16}$ of the weight of oxygen for the same volume, and their relative rates of diffusion are as 1 to 4. This appears to hold good in all cases.

With the apparatus shown in Fig. 10 the rate of interdiffusion of two gases may be observed. Place a little liquid in the gauges ; then blow, say, oxygen into one flask and hydrogen into the other. The liquid in the gauges will blow up to the bulb, and, after thoroughly
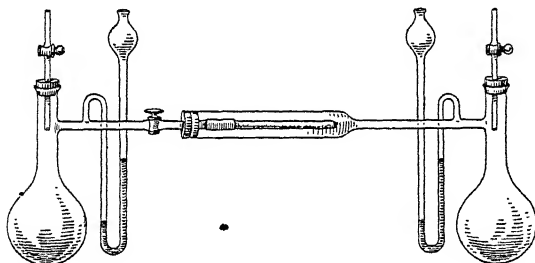
FIG. 10.

filling the flasks and closing the taps, the liquid will again fall into the tube and seal the gas. A momentary opening of the taps will level the gauges, and then the tap on the joining tube can be opened, thus allowing the gases to come in contact through the porous clay tube. It will be observed that the gauge on the hydrogen flask will slowly fall, whilst that on the oxygen will rise, indicating that more hydrogen is going through the porous tube into the oxygen than in the reverse direction. After some time both gauges will come to a common level. There will then be equal amounts of each gas in each flask, and as much is passing one way as the other.

Diffusion is, then, only to be explained by assuming that the minute particles or molecules of gases are in rapid motion, their velocity depending on their mass or weight and the agitating cause being heat-energy. *Cooling* a gas reduces the velocity of motion of the molecules, which accounts for diminution in pressure.

By means of diffusion it is possible to separate one gas from another, provided there is a little difference in density. For instance, if a mixture of hydrogen, oxygen, and nitrogen be conducted from one vessel to another by means of a length of, say, 20 centimetres of tobacco pipe (unglazed earthenware) much hydrogen will be lost on the first passage, and on repeating this treatment it can be entirely removed.

Glass and a number of substances known as colloids are quite non-porous. Although the ultimate particles of gases are extremely small, they are unable to penetrate glass even under great pressure. Unglazed earthenware, thin plates of some metals, and other substances are porous—that is, full of minute tubes or passages through which gases can easily pass or wander. If a mixture of two gases comes in contact with a wall of such porous material the particles will, if of the same weight or specific gravity, be moving at the same rate, and will hit and penetrate these passages or tubes at the same rate. The part passing through the porous barrier will have the same relative composition as at the beginning. But if one gas be lighter than the other its particles or molecules will be moving much quicker. It has therefore several chances to one over the heavier, depending on their relative densities, of getting through one of the fine tubes or pores.

The mechanism of diffusion goes some way to explain the nature of the gaseous state.

CHAPTER II.

RUSTING OR OXIDATION OF METALS.

MOST metals tarnish or rust slowly in air at ordinary temperature. This rusting usually takes place more rapidly when the metal is heated somewhat strongly or melted.

Rusting is generally due to some chemical action at the surface. Most often it is a case of absorption of oxygen. There is always a decided gain in weight when this is taking place. The process can proceed only to such an extent that a definite oxygen compound will have been formed.

Weigh a small porcelain dish. Place in it some copper turnings and weigh again—the amount of turnings may be between 1 and 2 grms. Heat the dish over a Bunsen flame, so that air has free access to the turnings. The copper will become black on the surface, and if the heating be patiently continued the whole of the metal will be converted into a reddish black powder. On weighing the dish again after cooling the copper will be found to have increased by almost a fourth of its original weight.

This experiment may be repeated with the metals tin, lead, and zinc. As all these melt under the conditions of heating, they become coated with a layer of dirty coloured material which protects the metal beneath. They should be stirred with a small glass rod, which is weighed along with the dish in the first instance, and, of course, left in the dish and weighed with it finally. A decided gain in weight in each case will be noticed. The products obtained should be saved for further experiments. They are oxides.

The two metals magnesium and aluminium may be similarly experimented with, but require more care.

Weigh a small porcelain crucible and lid. Take about 2·5 grms. magnesium filings, or 2·5 aluminium powder. Both these metals may be set on fire by a match flame. They will then glow very brightly, and the magnesium may give off a little fume or smoke. The magnesium will increase to about 4 grms. and the aluminium to about 5

With the metals mentioned the actions, when completed, can be expressed in chemical formulæ which represent definite amounts by weight acting together.

COMPOSITION OF AIR.—A rough idea of this may be obtained

copper turnings or fine wire contained in a tube (see Fig. 11). The flasks should be as nearly as possible the same size, or their capacity ascertained pretty accurately. One flask is full of air, the other of water. As the water flows slowly down the first syphon, air is driven over the metal contained in the heated tube, and displaces the water in the end flask. The second flask will not contain quite the same volume of gas as the first contained water.

Before measuring the water remaining in the second flask accurately, the cork with tubes should be rapidly replaced by another unbored cork, and at least two experiments made with the gas. First a lighted taper immersed for a moment; it will be extinguished. Then a burning piece of magnesium ribbon may be introduced; it will be seen to glow for a little time, but not actually burn with a flame. This gas
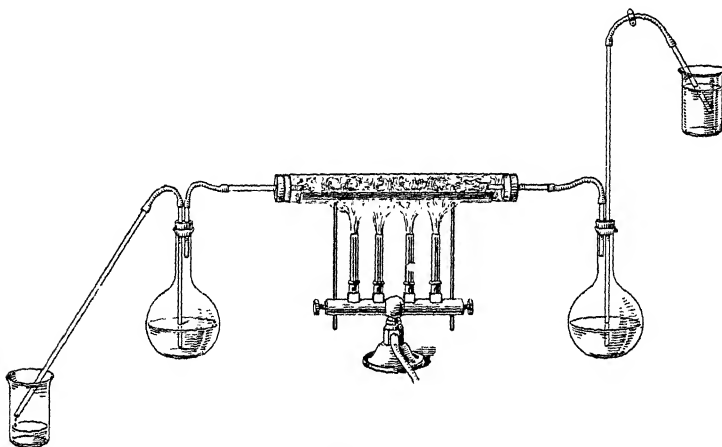
FIG. 11.

is mainly nitrogen. Ordinary combustible substances, as a taper, will not burn in it; but a few metals, magnesium and some others, will do so if strongly heated to begin with.

Now the water in the flask may be measured in a graduated vessel and an idea of the volume of oxygen absorbed by the red-hot copper obtained. If the capacity up to the mark was 1000 c.c., about 200 c.c. of water should be left if the volume of air driven over was also 1000 c.c. It may be less, because the gas is heated and expanded in passing over the red-hot copper.

Nitrogen obtained from air by any method of absorbing the oxygen is never pure, but contains argon and other gases.

Pure nitrogen may be obtained from several compounds. The most common natural compounds commercially obtainable are potassium and sodium nitrates. One or other of these nitrates is the immediate source of many nitrogen compounds.*

* Many plant and animal products, also coal and jet, contain small quantities of nitrogen in combination.

Nitrates contain a metal, oxygen, and nitrogen. They are somewhat complex substances. Potassium nitrate contains nearly, and sodium nitrate more than, 50 per cent. by weight of oxygen. When strongly heated both substances first melt and then begin to decompose, giving off gases, most of which is at first oxygen, and later a mixture of oxygen and nitrogen. If melted up with some metals the oxygen is retained as a solid compound and the nitrogen set free as gas.

Iron, in filings, is very suitable for this purpose. A thorough mixture should be made of dry powdered potassium nitrate (nitre) and iron filings, in the proportion of one part by weight of the nitrate to at least three of the filings.

The mixture should be placed in a tube of hard glass, arranged as in Fig. 12, and heated at first at the top part. The mixture will begin to glow and gas escape from the tube, and the glow will
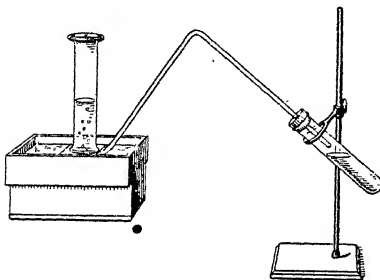
FIG. 12.

slowly extend down the tube. Several tubes must be ready to be filled. The water should contain a little sodium hydroxide, because iron filings may contain some carbon, which gives rise to carbon dioxide. The first tube full of gas is usually rejected, as it will contain some air.

The speed of the reaction can be modified by the amount of iron filings employed. The more filings the slower the action, and *vice versa.* With too small an amount of iron filings the reaction becomes an unmanageable fireworks. 10 grms. of saltpetre and 30 of iron filings will give quite sufficient gas to experiment with.

Other metals besides iron may be employed, but in some cases the action is somewhat ungovernable, and some oxides of nitrogen may be mixed with the product.

Larger quantities of nitrogen may be prepared by the reaction between some compounds of ammonia and nitrites.

Sodium nitrite and ammonium chloride give a good example of two compounds interacting.

Equal weights of these substances, say 10 grms. of each, are mixed with about 50 c.c. of water in a flask, with either side tube or cork and delivery tube. On gently warming, the reaction commences, and the nitrogen gas may be collected in any convenient manner, as in several tubes over water.

If a gas-holder is available a larger quantity of the gas should be collected. A gas-holder may be extemporised from a washing flask, as shown in Fig. 13.

The flasks and tubes are filled with water. The gas generator is attached by a flexible tube to the upright flask. As the gas enters
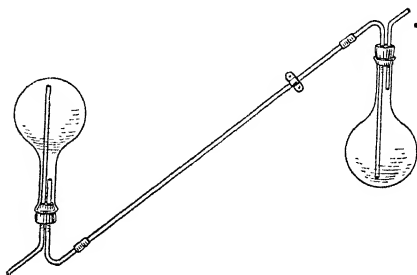
FIG. 13.

this the water flows from the inverted flask. The flexible tube on the upright flask must have a clip or stopper. If now water be driven into the inverted flask, the gas can be expelled at any desired rate from the upright flask and collected in test-tubes for experiment.
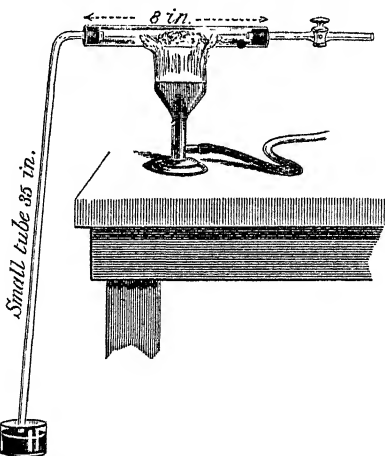
FIG. 14.

Experiments with the Tubes of Nitrogen Gas.

I. Test one tube with strips of blue and red litmus paper or with a water solution of litmus. They should not change.

II. A lighted taper is extinguished.

III. A glass rod dipped in lime or baryta water and held in the gas should not become white or milky.

IV. Make a fair amount of nitrogen gas and collect in some form

of gas-holder. A sufficient quantity may be obtained by mixing about 10 grms. of ammonium chloride (sal ammoniac) with the same weight of sodium nitrite, and warming with a little water in a flask with cork and delivery tube.   Arrange a tube containing a few grams of magnesium filings as in Fig. 14.   Drive the nitrogen slowly through a sulphuric acid drying tube, and then the magnesium tube to expel all air.   Then close the tap and heat the magnesium. The nitrogen will be gradually absorbed by the metal and the mercury rise from the cup up the tube.   The nitrogen may be again turned on and the operation repeated several times.   A nitride of magnesium is formed.   It is a red-coloured substance when hot and yellow on cooling.   It should be saved for further experiments.   On contact with water, magnesium nitride produces ammonia and magnesium oxide.   A very small quantity of this nitride is produced
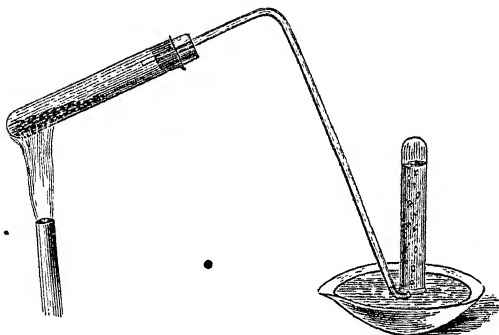
FIG. 15.

when magnesium ribbon is burnt in air.   The main product then, however, is magnesium oxide.

If the nitrogen from air be treated with magnesium somewhat on this line, but a little more elaborately, the inert gases, argon, &c., may be obtained as a residue not absorbed by the metal.

OXYGEN.—It is possible to separate oxygen from air, but not very easily, as most substances combine with the oxygen.

Most metallic oxides, when heated to a certain temperature, absorb a further quantity of oxygen, to a definite extent, producing another oxide.   At higher temperatures this new oxide will again decompose into oxygen and the original oxide.   By variations of temperature, therefore, it is possible to have a seesaw action—absorption at one stage and resolution at another.*

Red oxide of mercury may be heated in a tube something like Fig. 15.   Mercury will be observed to condense on parts of the tube, and a gas will collect over the water.

* This has been utilised for technical purposes—the production of oxygen on a large scale—barium oxide being the substance generally employed.   It is somewhat difficult on a small scale, and other methods should be first tried.

The tube should be of hard glass, as the temperature required will melt an ordinary test-tube. 1 grm. of the red oxide is sufficient for one experiment.

Test-tubes will generally do for collecting gases in these experiments. The tube should be about two-thirds filled with the gas, and then turned up, with the finger closing the tube, or a cork, previously prepared to fit, put in before taking from the water vessel. Care must be taken that on ceasing to heat, or on cooling, the water does not enter the hot tube.

The easiest and most commonly employed method of obtaining oxygen on a small scale is to heat a mixture of the substances potassium chlorate and manganese dioxide. It scarcely matters in what proportion the two are mixed. Each should be in powder. 10 grms. of the chlorate and 5 grms. of the manganese oxide is sufficient at one time. The manganese dioxide will be found practically unchanged after the operation, and may be obtained again by washing the residue. Other proportions of the ingredients may be tried. The chlorate, when heated alone, melts and gives off oxygen, but requires a higher temperature than the mixture, and the gas is liable to come off very rapidly; and, worse still, the leading tubes are liable to choke with particles of the chlorate, which may cause a dangerous explosion.

Manganese dioxide, alone, when heated to full redness, gives off oxygen.

Lead dioxide—the active substance of storage cells—gives off oxygen when quite gently heated. The tube arrangement in Fig. 15 can be used for this. Two or three grams of lead dioxide is a convenient amount.

Solid potassium permanganate may also be used in the same apparatus, but is very liable to stop up the leading tube by spirting.

All the methods above mentioned of obtaining oxygen are dry reactions. A considerable number of methods are known in which *solutions* of substances in water are employed. A very interesting one depends on a seesaw action between oxide of cobalt and bleaching powder.

To a mixture of bleaching powder and water a very small quantity of any cobalt compound—the nitrate or chloride—is added, and a black oxide of cobalt is produced, which undergoes decomposition and is again formed, and so on, with the result that a steady output of oxygen gas is obtained. The mixture froths up somewhat, so the operation should be performed in a moderate sized flask. The addition of a little thick paraffin oil diminishes the frothing, but is required only when the operation is on a somewhat larger scale. A small flask may be substituted for the test-tube in Fig. 15 for the cobalt oxide experiment.

Experiments.

I. Introduce into one tube of the gas a small piece of charcoal held in a wire. The charcoal should be just started glowing at a point. It will commence to burn very brightly. Or a splinter of wood on

which is a glowing spark—not a flame—may be used instead of the charcoal.

II. Coil up a very thin iron wire, such as flower wire, into a spiral two or three inches long. Dip one end in a little wax or paraffin. Start this burning, and introduce into a tube of oxygen. The iron will commence to burn brightly, and drops of oxide of iron may form.

III. Test one tube of gas with moist blue and red litmus paper and also iodised starch-paper. None of them will be affected if the gas be pure.

Quite a number of compounds absorb oxygen without the appearance of burning. This absorption happens, of course, with air as well as with pure oxygen. This may be shown by having a test-tube with well-fitting cork and tube as in Fig. 16. Fill the tube with oxygen. Introduce rapidly two or three cubic centimetres of a strong solution of pyrogallol made alkaline with sodium or potassium hydroxide.
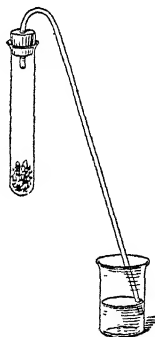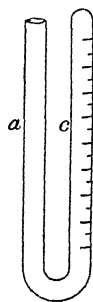
FIG. 16.   FIG. 17.

Close quickly with the cork and tube; dip the open end of the tube in water. On shaking the test-tube the oxygen will be absorbed, and the water will rise and overflow into the test-tube.

Other liquids, as an aqueous solution of ferrous oxalate, and especially a solution of cuprous chloride in ammonia, may be tried in the same way.

A rough analysis of air can be made by means of a bent tube and one of these oxygen-absorbing liquids (see Fig. 17). Commencing with the tube dry and full of air, put in sufficient water to just enclose the air in the limb c and be the same height in both limbs.

If the tube is not graduated, mark the level of the water by attaching a strip of label. Then pour into a a strong solution of pyrogallol and sodium hydroxide. Put a few drops of oil on the top of liquid in a. Allow the tube to stand, with now and then a gentle shake, for some time, until the volume of air in c no furthur diminishes. Then withdraw, by means of a tube, some of the liquid from a until the liquid is the same level in each limb. The gas will then be under atmospheric pressure. Mark the level or read off the graduation. The volume absorbed should be about a fifth of the

original. The tube may be left for a day or two, provided a layer of oil is on the surface in *a*. Ordinary petroleum or lamp oil will do for this purpose.

OZONE.—This substance is a modification of oxygen caused by some internal rearrangement in the substance. It is generally called an allotropic form of oxygen, and may be produced in several ways from oxygen.

The simplest method of production is by the passage of quiet electric discharges through oxygen or air.

A simple apparatus consists of a glass tube, about 25 or 30 centimetres long and 1 centimetre, or less, in diameter, through which a platinum wire is passed, either straight or spirally, and a little copper wire wound around the outside. The inner platinum and the outer copper are respectively connected to the two terminals of a small induction-coil. On sending a feeble current through the coil there will be a silent discharge between the inner and the outer wire through the glass and the air space.

If air or oxygen be blown through the tube some of the oxygen becomes converted into ozone, which can be recognised by: (1) Its odour; (2) if blown on some iodised starch-paper a blue colour will be produced; (3) if blown on to a little very clean mercury the metal will tarnish and cease to run so easily; (4) blown on a piece of clean silver foil it will produce a dark brown stain.

These actions are all cases of direct oxidation, produced, as supposed, by the ozone reverting into ordinary oxygen and at the same time imparting oxygen to the substances mentioned.

This *modification* is much more active as an oxidising agent than ordinary oxygen, most metals and many other substances being oxidised simply on contact with it at ordinary temperatures. Ozone is doubtless produced in many other ways: by the electrolysis of dilute sulphuric acid—when a small blowpipe flame is supplied with excess of air—and when some substances are undergoing a slow or partial oxidation. For instance, phosphorus in moist air slowly oxidises at the ordinary temperature; an odour like ozone is imparted to the surrounding air and iodised starch-paper and other reagents are affected in the same way as by the ozone from the electrified tube.

CHAPTER III.

THE COMPOSITION OF WATER AND PREPARATION
OF HYDROGEN.

A NUMBER of metals become rusted on contact with water—some at the ordinary temperature, others in contact with steam or at higher temperatures.

Several pieces of clean metals should be placed in a tube and subjected to a current of steam for a few minutes, and the surfaces of the metals examined. Scrape with a knife or clean with sand-paper strips of aluminium, zinc, copper, iron, magnesium, lead, tin, &c.; place in a wide tube and drive steam over from a flask.

This may be done with the metals separately or together. It is better, however, that they do not touch, so that no electric couple is formed.

It will be found that of the metals mentioned the magnesium will tarnish first and to the greatest extent, followed by zinc, lead, iron, aluminium, about in this order, and that copper and tin will show no signs of change.

The water should be boiled for at least ten minutes and the steam allowed to escape before the metals are introduced into the tube, to avoid the effects of air and carbon dioxide, which are always contained in solution in ordinary waters.

FIG. 18.

This tarnishing in steam is due mainly to the same cause or causes as tarnishing on heating in air—that is, oxidation.

Boil some water in a flask, and when steam is escaping freely introduce a little bundle of burning magnesium ribbon. It will continue to burn in the steam, and even on the surface of the boiling water, and a very pale flame will be seen at the mouth of the flask (see Fig. 18).

A white powder will be formed in the water, and may be separated therefrom by filtering. This powder is magnesium oxide, and, if examined, will be found to behave exactly like the white powder obtained by burning this metal in air or oxygen.

The following experiment will be instructive as to the action of some common metals on steam at a moderately high temperature (see Fig. 19).

A little of the metal, in filings or small pieces, is placed in the tube C (a coil of galvanised or zinc-coated iron wire will be found to work excellently). Water is boiled briskly in the flask A, and the steam allowed to expel all the air from the tube before placing the tube D over the end of C. The tube and metal must then be heated, carefully at first and finally strongly. The steam will condense in the water and carry some uncondensable gas with it. This will collect in the tube D. Zinc and iron will be found to be most active, and copper will not be acted upon in the least, even if red hot. The tube C is liable to crack if drops of water condense in it. The steam can be stopped almost at once by raising the safety tube B.

Examine the gas collected over the, now warm, water, by closing the open end under water with the finger or a cork, as before men-
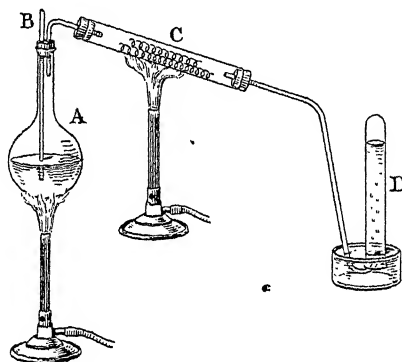
Fig. 19.

tioned, bringing upright quickly, and applying a lighted taper. The gas should ignite with a slight puff and an almost invisible flame. This gas is hydrogen. It can be obtained from water by several other methods, but most, if not all, are indirect ones. Powerful electric sparks, when passed through steam, decompose it into two gases, hydrogen and oxygen, which may be collected together. This experiment is not a simple one. It requires a large induction-coil to produce a stream of sufficiently powerful sparks, and an arrangement something like Fig. 20, which consists of a steam-producing flask, a flask with side tubes to allow the entrance of platinum wires through corks, an outlet for the steam and gases, and a safety outlet with tap. Steam is first driven through the flask until the bubbles are completely condensed by the water in the dish. Then contact is made with coil, and sparks pass across the current of steam. Some is decomposed and the products carried forward into the tube. This tube may afterwards be inverted and a flame applied to the collected gas, which will now explode with a sharp report.

The gas can, by diffusion experiments, be proved to be a mixture of oxygen and hydrogen.

It is perhaps impossible to decompose pure water by an electric

current, but when the water contains an acid or some of the compounds called " salts " in solution it may be decomposed and one or both gases obtained. This action is generally spoken of as the *electrolysis of water.** If the current from two or three cells—say storage cells—is led by means of two platinum wires or strips into water containing a little sulphuric acid the wires or strips will become covered with small gas bubbles (see Fig. 21). If tubes full of water be inverted over the wires or " terminals " the gases will rise and collect in them. After sufficient has collected the gases may be examined by applying a lighted taper to each in succession. The contents of one tube will inflame, and the other will cause the taper to burn more vigorously. The latter is oxygen, and on examination will be found
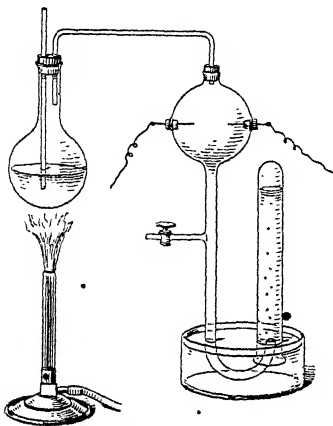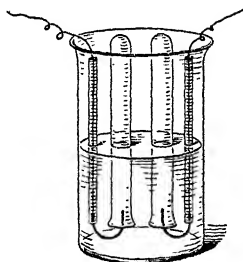
FIG. 20.   FIG. 21.

to have collected at the terminal from the positive or red-marked end of the storage cell. It will be noticed that the volumes of the gases are not the same. The volume of the hydrogen will be nearly twice as great as that of the oxygen.

To get this result it is necessary to use platinum or some metal that does not easily oxidise or combine with oxygen. If, for instance, the current is led into the acid water by two plates of lead there will be very little gas escape from one plate, but the plate will become brown coloured owing to the formation of a lead oxide. The other plate will have hydrogen bubbles given off at its surface, just like one of the platinum plates. Gold and silver behave like platinum, and most of the common metals somewhat like lead.

An accurate knowledge of the composition of water is of the greatest importance in chemistry. Water, in fact, may be considered in several respects as a standard substance. On its composition by weight and volume, and therefore to some extent its constitution,

* The nature of the substance dissolved in the water has a considerable deciding effect, ammonia, for instance, not acting in the same manner as sulphuric acid.

the formulæ or composition, from a purely chemical point of view, of all other compounds are based and expressed. Electrolysis yields, as stated, almost exactly two volumes of hydrogen to one of oxygen. From reliable experiments, oxygen is sixteen times heavier than the same volume of hydrogen, when they are both under the same physical, conditions. When the two gases, in the purest possible condition, are mixed together and induced, by heat or an electric spark, to combine, they do so exactly in the proportion of two volumes of hydrogen to one of oxygen, and if the gases in the mixture were not in this precise proportion the excess of one or the other would be left untouched.

Supposing two volumes of hydrogen and one of oxygen to be confined in a suitable vessel at a temperature at which water is steam or gaseous—that is, some temperature above 100° C. (it is quite indifferent how much above this point, within reasonable limits)—and the mixture exploded. The product will then be steam, and its volume is exactly two-thirds of the original volume of the gases—that is to say, two volumes of hydrogen combine with one volume of oxygen to produce two volumes of steam at the same temperature. A contraction is therefore noticed.

Thus the steam, obviously a compound, is the same in volume as the original hydrogen.

There is a great change of volume from water into steam, one volume of water giving 1680 volumes of steam (or one cubic inch giving very nearly one cubic foot of steam at the same temperature).

Stated another way, 1 grm. of hydrogen and 16 grms. of oxygen each occupy the same volume—viz., 11,200 c.c.—at 0° C. and 760 mm. bar. Therefore, if we could obtain steam at 0° C., in 18 grms. of it 16 would be oxygen and 2 hydrogen, originally occupying 33,600 c.c., but now of the volume 22,400 c.c.

The figures 2 and 16 represent the ordinary combining proportions of hydrogen and oxygen respectively.

The chemical formula H_2O is intended to indicate that the substances hydrogen and oxygen are contained in proportion by volume of two to one, and by weight of two to sixteen, and that this is the smallest possible expression for the entity steam when something of the idea of atoms is taken into account.*

Other Sources of Hydrogen.—Besides water, quite a number of substances contain hydrogen. Some of these give up the whole or part of the hydrogen in contact with certain metals.

* The atom, from the chemical point of view, is an exceedingly small piece of matter ; it is the smallest piece that can enter into any kind of chemical engagement. It is not identical with the electrical notion of ions.

The chemical atoms of different materials are supposed to be of the same size or volume, but differ in weight. As to shape nothing can be said.

Taking masses that are measurable of hydrogen and oxygen, their weights per equal volumes are as 1 to 16. Presumably the atoms making up any mass or volume, as 100 c.c., are also as 1 to 16. These values may be called their relative atomic weights.

The idea of atom and atomic weight involves some unit. This matter is not quite simple. Hydrogen is certainly the lightest substance known. Compared with it, oxygen is quite sixteen and nitrogen fourteen times as heavy,

Of these, generally speaking, "acids" are the most active. Many acids are formed by the union of some *oxides* with water. For instance, sulphuric, phosphoric, and nitric acids result from oxides having combined with some water. Other acids, as hydrochloric, &c., are simpler in their nature, consisting of hydrogen and one other element. These often dissolve in water, giving solutions which possess many properties similar to those of the former class.

A considerable number of metallic oxides are able to combine with water to form "hydrates" or "hydroxides." Some of these hydroxides can be attacked by certain metals, in which case hydrogen is always expelled.

Most metallic oxides have also the property of being able to combine with acids to form a class of substances called salts. It is a very numerous family or class. Acids, when dissolved in water, exhibit the

bulk for bulk. Presumably the atoms, or ultimate particles, as they also have been called, retain this weight relationship.

The atomic weight can be directly determined in but a few cases, by comparison with hydrogen.

It is quite a fundamental matter in chemical actions and undoubtedly always true that when substances join to form a compound or any chemical changes of any kind take place the quantities of matters involved in the changes are in the proportions of these atomic weights or some simple multiple of them. In the case of water the conventional symbol expresses that *two* atoms of hydrogen are linked in some way with one atom of oxygen. The one atom or piece of oxygen by volume may therefore be considered as in some way equivalent to two pieces of hydrogen. By weight, sixteen of oxygen are equivalent to two of hydrogen; consequently one atom of oxygen is "equivalent" to two of hydrogen, and 16 : 2 are their respective combining or equivalent weights.

Comparatively few substances combine with hydrogen, but oxygen and chlorine and one or two other of the elementary substances have a considerable range of activity. They will join not only with hydrogen, but with nearly all the other elements with more or less ease.

For instance, copper and hydrogen do not, properly speaking, combine, but copper and oxygen do so most easily.

The compound produced when a certain quantity of copper has taken up as much oxygen as it can consists of 63 parts by weight of the metal and 16 of oxygen. Therefore in the 79 parts of oxide of copper the 63 of metal must in some way be doing the *same extent* of work as the 2 parts of hydrogen in 18 parts of water. It cannot, of course, be doing quite the *same kind* of work, and there are very different amounts of energy produced or involved in the formation of the respective compounds, but it is evidently, as far as quantity is concerned, equivalent.

Now this "equivalence" is evidently able to change. If this particular oxide of copper, containing 63 parts of metal to 16 of oxygen, be heated to a certain temperature (and by some other means) it will be changed in colour, texture, and composition. Exactly half the quantity of oxygen will be left in it, or double the quantity of copper. They are now as 63 to 8 or 126 to 16. Either way the equivalence of the copper has altered, so that 63 is now equivalent to 1 of hydrogen.

The compounds here alluded to are expressed as CuO and Cu_2O
$63+16$ $126+16$
respectively.

Another compound of hydrogen and oxygen is known in which the relative equivalence of hydrogen and oxygen is as 1 to 16. This is the peroxide of hydrogen, H_2O_2. In a number of cases where equivalence thus changes one compound will be of a much more stable and resistant nature than the other. The substances just named are good examples of this.

property of changing many vegetable and other colours. Thus blue litmus is turned red by acids.

Salts, as a rule, have little or no action on vegetable colouring-matters. As all salts are in part made up of acids, and as the power of changing colours has vanished in the salt, it follows that the other portions of the salt must have the power of overcoming or destroying this property of acids. Only a few metallic oxides are capable of dissolving in water to any considerable extent, but if a solution of any oxide in water (*e.g.*, oxides of sodium or calcium) is tested with a vegetable colouring-matter the solution will be found to have the power of altering the colour in the reverse direction to that of the acid.

A substance whose solution has the power of changing colouring-matters in the reverse way to that of an acid is called an " alkali," and we can now see why most salts, being made up of substances of opposite properties, have no action on vegetable colours, or, in chemical language, are *neutral*. The alkaline character of many metallic oxides cannot be shown, as no aqueous solution can be obtained, but the property is latent, as they show the same property of neutralising acids as the alkalis or soluble oxides. Hence an alkali is nothing more than a metallic oxide that happens to be soluble in water, and therefore able to show its action on colours directly.
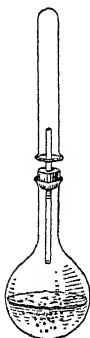
FIG. 22.

HYDROGEN FROM METALS AND ACIDS.—The statement that metals expel hydrogen from acids is probably correct in all cases, but to obtain hydrogen practically it is not advisable to take any acid or metal on chance, because some secondary actions may take place.

Sulphuric Acid and Zinc or Iron.

In a flask of about 500 c.c. capacity place 200 c.c. water. Pour into this not more than 20 c.c. of strong sulphuric acid. The mixture of acid and water will become moderately heated, owing to the sulphuric acid combining with some water. Now drop into the acid some clean zinc, in clippings or granulated, or pour the acid solution on to some zinc mixed with water. Water must never be added to sulphuric acid, as the temperature may rise so much that some acid may be projected.

The surface of the metal will almost immediately become covered with small gas bubbles. These will rise to the surface of the liquid, and after a short time the contents of the flask may become heated and bubble violently. The action can be moderated by external cooling, dipping into water or holding under a jet of water.

A cork fitted with a moderately small-bored glass tube of 12–15 inches length must be provided beforehand. After the action has gone on for a few minutes, the cork and tube is inserted, and the gas permitted to displace all air before any gas is collected. A flexible tube may be attached to the glass tube and the gas collected over

water, or simply by holding inverted tubes over the outlet, letting the light gas displace the air.

Instead of zinc, iron in wire or filings may be used; or nickel or aluminium, both of which may be obtained in wire or thin sheet, should be tried. The gas evolution will be observed to be much less active in these cases than with zinc.

The "strength" of the sulphuric acid solution has a decided effect on the *rate* of evolution of gas, whatever the metal may be. This may be seen by making some dilute acid—say 1 c.c. of the acid and 200 c.c. of water—and trying the effect of this on zinc. An action will be observed, but little gas will collect compared with the previous case.

Now place 20 or 30 c.c. of the concentrated acid in a small flask, and add the zinc to this. Gas bubbles may appear on the surface of the metal, but no evolution of gas will be observed. On carefully heating to a moderate temperature the zinc will begin to dissolve, a whitish cloud will appear in the liquid and gases will begin to come off. These gases are not hydrogen, but some sulphur compounds.

On some of the other metals, as iron or aluminium, the pure concentrated acid has little or no effect. Iron and aluminium vessels are, indeed, sometimes used for holding the strong acid.

The action between the zinc and acid, as first mentioned, may cease owing to all the metal being dissolved or all the sulphuric acid removed by the metal. If the metal disappears, make sure that all the acid is used up by adding more metal. Pour the solution into an evaporating basin and boil down to about half the original bulk and put aside to cool. Crystals of zinc sulphate should form. Crystals are sometimes slow to form even from concentrated solutions. In such cases a few drops evaporated on a slip of glass and well stirred with a glass rod or match will generally give a crystalline residue, and this, agitated with the concentrated solution, starts, as a rule, the crystallisation. In a case of this kind the temperature of the solution before and at the time of formation of the crystals should be noted. Supersolution or superfusion takes place with many substances, probably with all under suitable circumstances. When this happens there is always a rise in temperature when the matter assumes the solid state, whether it be from a solution or from a melted material.

From the final results of the action of zinc and sulphuric acid on each other it is found that for every 98 parts by weight of the acid used 65 parts of zinc are dissolved and are contained in the zinc sulphate produced, and 2 parts by weight of hydrogen are given off. The hydrogen has, relatively to the zinc and acid, an enormous bulk. Supposing the "parts" were grams, the hydrogen would have a volume of more than 22 litres. The 98 parts by weight of the sulphuric acid are made up of 32 parts sulphur, $4 \times 16 = 64$ parts oxygen, and 2 parts hydrogen.

The zinc sulphate, as obtained in crystals from the solution, contains water of crystallisation.

If these crystals be heated, or the solution of the zinc in the

acid and water be boiled down and then strongly heated, a white powder will be obtained which is the real dry zinc sulphate. Based on the above, the action between zinc and this acid can be shown as a chemical "equation" by using symbols and formulæ.

$$Zn + H_2SO_4 = H_2 + ZnSO_4.$$

$$\begin{matrix} 65 & 98 & 2 & 161 \end{matrix}$$

$$\left.\begin{matrix} 65 \\ 98 \end{matrix}\right\} = 163 \qquad \left.\begin{matrix} 2 \\ 161 \end{matrix}\right\} = 163$$
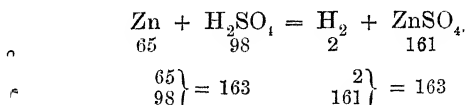
Many other acids behave similarly, but practically the only one used, besides sulphuric, for this purpose is hydrochloric acid.

This acid differs considerably from sulphuric. It is a solution in water of a gaseous compound of chlorine and hydrogen, and contains no oxygen. Ice-cold water will dissolve several hundred times its volume of the gas. On this solution being heated much of the gas is expelled, but simple boiling will not expel the whole
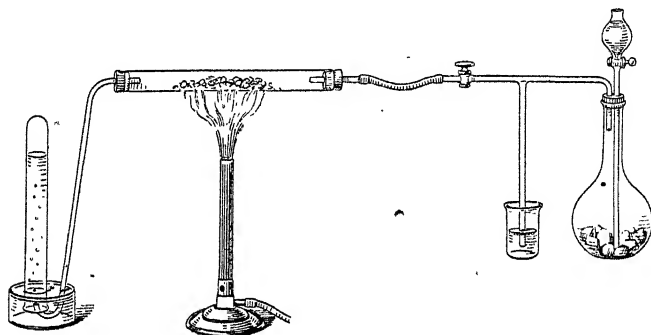
FIG. 23.

The flask contains 200–300 grms. of common salt—sodium chloride (or about the same quantity of sal-ammoniac). The dropping funnel contains strong sulphuric acid. When these compounds come in contact an interchange of elements takes place, sodium from the salt becoming united to the sulphuric acid and hydrogen from the sulphuric acid joining with the chlorine of the salt to a certain stage, as expressed by the equation $NaCl + H_2SO_4 = NaHSO_4 + HCl$,
Salt
the process requires no external help by heating. The glass into which the safety tube dips contains a little sulphuric acid.

of the gas. The ordinary acid is a slightly coloured liquid which fumes a little on exposure to air.

Zinc and several other metals dissolve more rapidly in this acid than in sulphuric. The reaction between hydrochloric acid and the metals aluminium and magnesium is a very energetic one, and quickly becomes almost unmanageable when the strong acid is used.

Tin may be used, the action not being violent unless the acid is strong and heated.

Hydrochloric acid may sometimes be employed in the gaseous state with advantage. In this condition the rate of action can

be regulated and the nature of the metallic element is of less consequence.

The apparatus required for the preparation of hydrogen from a metal and the gaseous hydrochloric acid is shown in Fig. 23. The metal is placed in the wide tube, which should be of good glass, and heated, in the case of zinc or tin, until the metal melts. Iron or aluminium, if in filings or turnings, need but gentle heating. The speed of output of gaseous hydrochloric acid can be regulated by the rate of dropping of the sulphuric acid on the salt, and also by the tap, any excess escaping through the safety tube. The metal may also be contained in a small porcelain boat.

The final results of this action, in the case of zinc, can be expressed by:

$$Zn + 2HCl = H_2 + ZnCl_2.$$
$$65 + 2 \times 36·5 = 2 + 136$$
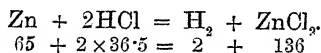
The product formulated as $ZnCl_2$,—zinc chloride—will be seen, in the experiment with the gas, to form as a clear liquid around the melted zinc and to vapourise slightly along the tube. If other metals than zinc be used a chloride is also formed, but will be very different in appearance from the zinc compound. When zinc is dissolved in the ordinary liquid hydrochloric acid and the solution heated until the water is expelled the same compound is left. This also applies to other metals dissolved in the aqueous acid.

Acids are not the only substances from which hydrogen may be obtained by the action of metals. The hydroxides of metals contain hydrogen which can be displaced by metals. The two most soluble hydroxides are those of sodium and potassium, and several of the more common and abundant metals, as zinc and aluminium (and also magnesium and calcium), react in an energetic manner with them, driving off hydrogen.

Dissolve about 5 grms. of sodium hydroxide in 100 c.c. water, contained in a flask. Add about the same weight of aluminium, in foil or small pieces. (The temperature rises considerably, as a rule, and the flask may need external cooling.) Hydrogen is very rapidly given off. The gas prepared in this manner is not quite pure, but better than that obtained by the interaction of iron and an acid. For the common reactions the small quantity of impurities will not seriously interfere.

The metals sodium, potassium, and magnesium decompose water more easily than any other substances. The final products are hydrogen and hydroxides of the metals. The dry hydroxide of sodium, &c., gives off hydrogen on contact with metallic sodium, &c., but the action is not rapid until the hydroxide or the metal melts, and is not a practical or safe method of preparing hydrogen.

Considerable danger always attends the employment of potassium or sodium in the metallic state.

Experiments.

Owing to the difference between hydrogen and other gases in relative weight it can be collected by what is termed upward

displacement. That is, if a tube or bottle be held mouth downwards, and hydrogen be simply led in by a tube rising a little way inside, the air will be thrust down by the lighter gas. A litre of air weighs about 1·29 grm., whilst a litre of hydrogen under the same conditions weighs but ·0896 grm. That is, for the same volume the air is more than fourteen times heavier. Exactly, they are as 1 to 14·4.

After filling a tube with hydrogen, empty this under another inverted one containing air. The air will be displaced. This can be tested by applying a burning taper to the mouth of the inverted tube.

Collect several tubes in this manner, or in the usual way with some other gases, by water displacement. (N.B.—Some impurities are removed by water.)

I. Introduce into an inverted tube of the gas strips of red and blue litmus papers. They should be unchanged.

II. A lighted match or taper will be extinguished if pushed into
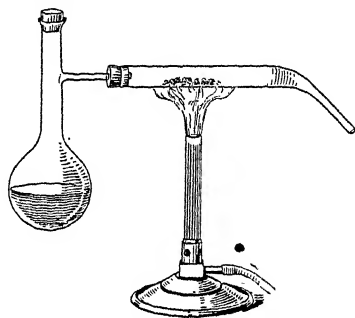
FIG. 24.

the gas, although the gas will burn in the air at the mouth of the tube.

Fire the gas at the mouth of a tube and hold a clean knife blade in the flame. It will be covered with dew or moisture.

III. A glass rod dipped in lime or baryta water and held in the gas will *not* become white or opaque.

IV. A coil of moderately small copper wire should be heated over a flame and introduced hot into the hydrogen in a tube. The copper will appear bright red where in contact with hydrogen, although black in the parts exposed to air.

This effect is due to the removal of the layer of oxide from the copper. Many metallic oxides when heated to some particular temperature in hydrogen give up part, or the whole, of the oxygen to that gas.

Place a few grams of red oxide of mercury in a tube of about 20 cm. length (see Fig. 24). Lead a gentle stream of hydrogen gas through the tube from any form of generator, and then apply a Bunsen flame to the part of the tube only where the oxide is. The oxide will appear to be burning, and mercury will condense in small drops and form a ring like a mirror a little way along the tube.

Further away water drops will be deposited, and a little condensing steam may be visible at the end of the tube.

A quantitative experiment should be performed in the same apparatus, employing another metallic oxide. The oxide of copper, formed by heating the metal in air until it ceases to gain in weight, is most suitable. The hydrogen should be dried by bubbling through a concentrated sulphuric acid tube (Fig. 25). The copper oxide can be contained in a small porcelain boat, or a boat may easily be made from clean copper foil by bending a small piece round a pencil and turning in the ends.

The boat is to be first weighed, and then charged with the oxide and again weighed. The quantity of oxide should be from 1 to 2 grms. Pure copper oxide consists of 63 parts copper and 16 oxygen, so that about 20 per cent. of its weight is due to oxygen. The tube shown in Fig. 25 is attached to the end of the tube containing the boat and oxide. This water-collecting tube contains a few c.c. of strong sulphuric acid. It is weighed before attaching. Firstly the whole tube is thoroughly filled with the dry hydrogen gas, and whilst a steady current is running the part where the boat lies is heated to redness if possible. The black copper oxide will change colour to red, and water may condense in the tube where cool. It can be seen when the reaction is complete by the change in colour. The heating must be maintained for some time after this, and the moisture driven into the sulphuric acid-catcher by warming the whole length of the tube. With the quantity named and a steady stream of hydrogen the operation should be completed within about forty minutes. The heating is discontinued, but the hydrogen current kept on for a little time until the tube is almost cold. The water absorber is then to be detached and weighed, and the boat, with its metallic copper, also weighed.
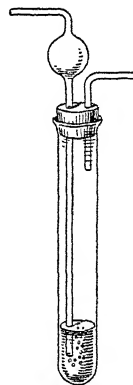
FIG. 25.

From this experiment the loss of weight of the copper oxide (n) gives the amount of oxygen used in producing the water formed and weighed together with the water absorber (m); $m - n$ gives the weight of hydrogen used in forming m grms. of water or combining with n grms. of hydrogen; $m - n/n$ will be found to approximate to $\frac{1}{8}$, which means that one part of hydrogen combines with eight parts of oxygen to form nine parts of water. The equation $CuO + {}^nH = Cu + H_2O + {}^{n-2}H$ can be based on this result.

The experiment can be simplified by allowing the steam to escape, weighing the copper oxide and resulting metallic copper only. In this case the copper oxide should be made by the student from metallic copper by heating in air until there is no further increase in weight.

Other metallic oxides "reducible" under these circumstances are the several oxides of lead (litharge, red lead, peroxide), zinc oxide, ferric oxide. The lead will appear as melted globules, the zinc as a

grey slightly metallic looking coating on the tube, and iron as a black powder which is attracted by a magnet and rapidly becomes reoxidised on exposure to air.

NASCENT HYDROGEN.—It is not always necessary to conduct the process of "reduction" by hydrogen at a high temperature. In a number of cases it is only necessary to liberate the gas *in contact* with the substance containing oxygen, &c. It is always quicker and more perfect when the substance to be reduced is soluble in the liquid employed.

The action is best seen when a liquid, as dilute sulphuric acid, is electrolysed, platinum plates being employed.

Examples.

Colour some dilute sulphuric acid by dissolving therein a little potassium permanganate. Arrange a small beaker with the solution and two strips of platinum foil as poles or electrodes. On connecting with a storage cell (or battery) it will be seen that the liquid around the pole at which hydrogen is liberated becomes decolourised, and scarcely any hydrogen bubbles will be perceptible until the colour has quite vanished.

Dilute acid coloured by a little permanganate may be decolourised by stirring with a piece of zinc or iron.

Also, if to a mixture of zinc and dilute acid in which hydrogen is visibly forming, a solution of a permanganate or bichromate or nitrate is carefully added, the gas formation will to some extent cease, and only recommence when a certain amount of oxygen has been taken away from the substances named. In cases of this kind the temperature always rises.

GALVANIC COUPLES.—Water can be decomposed so as to produce hydrogen by means of galvanic couples; but the output of the gas is not rapid or in quantity, as is the case with some methods already described.

Copper-Zinc Couple.

If metallic zinc be dipped into a solution of a copper compound, as the sulphate, blue vitriol, fine particles of metallic copper are deposited on the zinc surface, which appears black. It is not a very coherent coating, and may be rubbed off without difficulty. Each little particle of copper and the zinc beneath form a galvanic couple. To make this, the zinc in filings, turnings, or clippings of thin sheet metal, or even granulated metal, is first cleaned by boiling for a few minutes in weak sodium hydroxide solution, thoroughly washed with hot water, and then shaken up with a very weak (5 per cent.) copper sulphate solution until a fairly even black coating has formed. It is then quickly washed several times with cold water.

The result of the action of the many 'short-circuited couples is that zinc oxide, or hydroxide, and hydrogen are produced, the

copper not being affected.   Some other combinations, as platinum-zinc, platinum-iron, copper-magnesium, &c., are more active, but for most purposes the copper-zinc is effective.

A few grams of this copper-zinc couple boiled with water will give a small quantity of hydrogen.   The water will become cloudy, or a white coating will form on the couple when the action has gone on a little time.   This is zinc oxide or hydroxide.   Magnesium very slightly coated with copper or platinum decomposes water much more rapidly than the zinc combination.*

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* The purity of the hydrogen obtained *by any process* depends upon both metals and acid.   Iron and some other metals which contain carbon, and sulphur, &c., give off a very " odorous " gas, however pure the acids may be. The odour is due to carbon, or sulphur or phosphorus compounds of hydrogen, which are formed in very small amount as the metals are dissolving.   When perfectly pure hydrogen is required these impurities must be washed out by suitable means or the method of electrolysis employed.   When hydrogen is required in large amount, as for balloons, absolute purity is not necessary, and ordinary iron turnings and dilute sulphuric acid are the most convenient materials for its production.   Aluminium and sodium hydroxide are also convenient for this purpose, owing to the lightness of the metal, &c., for carriage.

CHAPTER IV.

CARBON AND CARBON COMPOUNDS.

THE substance known as carbon is almost as widely distributed as the three elements previously dealt with. It is found in the so-called elementary state as minerals—graphite and diamond—and in many mineral and countless organic compounds in chemical union with other substances, particularly oxygen, hydrogen, and nitrogen. As to quantity, the imagination can perhaps be helped by the statement that about 12 per cent. by weight of all chalk, limestone, &c., is carbon, and that it exists in all plant and animal products in still greater amount.

CHARCOAL is obtained by subjecting almost any kind of organic substance to a high temperature in such manner that little or no air can gain access to the material whilst it is being heated. Some substances, when heated, first melt, and at some higher temperature *decompose.* Carbon compounds are very numerous, and decompose at various temperatures and in various ways. Nearly all do decompose at high temperatures, and when this happens some of the carbon is released from its union with, it may be, hydrogen, or hydrogen and oxygen, &c., and is left or deposited in the vessel in which the heating takes place in the form of a *charcoal.* The external form and appearance of this charcoal as well as its composition depend on the nature of the carbon compounds employed and the temperature and duration of heating. In very few cases is charcoal anything approaching pure carbon, but very pure carbon may be obtained from charcoals by appropriate treatment. It is always non-crystalline and black in colour, but in hardness may vary exceedingly. Carbon does not melt or vapourise at any ordinary temperature.

Obtain some cellulosic material, either cotton-wool, flax, linen, wood-shavings, straw, &c. Heat these in a small retort or distilling flask, which should be arranged so that the gases and other products can be to some extent caught and examined (see Fig. 26).

The bulb of the retort may be three parts full of the material, and the heating carried on to the highest temperature the glass can withstand and until very little more gas is given off.

Some tubes full of gases may be collected, and each one examined as to its manner of burning, whether with a very luminous flame or one only slightly so.   The water in the funnel or trough should also be examined by red and blue litmus papers, as substances distil over and collect on and in the water.   Oily products of thick consistence and unpleasant odour will collect in the neck of the funnel and separate to some extent from the water.   The water will contain several things in solution, from which they may be extracted without much difficulty.

The retort must first be allowed to cool and then only removed, and broken to obtain its contents, which are "charcoal."   The charcoal will have the same shape as the original matter, but will be
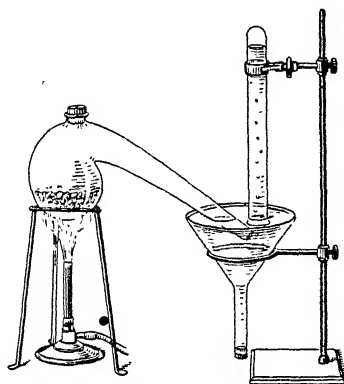
FIG. 26.

much reduced in size.   It and the original matter should be examined under the microscope.

Unless the temperature was very high and long continued, the charcoal made in a glass retort will be found to smoulder or glow in the air when just set fire to, until all the black material has gone and a little greyish powder is left.   The amount of this residue or ash differs materially in the substances mentioned, cotton-wool leaving least and wood or straw most.   The charcoals can easily be crushed to a very fine powder.   This powder is of about the same relative weight as water, so that when shaken up with water it sinks but slowly.   It is quite insoluble in water or other liquid unless there be some chemical action.   Hot concentrated nitric acid will often set this kind of charcoal on fire, and hot sulphuric acid will also be acted upon by it, but more slowly.

Some of the freshly made and powdered charcoal should now be shaken up with a little water to which litmus solution has been added until decidedly blue coloured.   On filtering off the suspended charcoal it will be noticed that the colour has departed from the water.   Freshly made and finely powdered charcoal attracts many colouring-matters from liquids.   It also, when dry, absorbs gases in considerable amount.

Wood charcoal can be made from any kind of wood or woody fibre. It differs a little in physical properties, according to the source. On a large scale it is made by heating wood in iron cylinders, or sometimes carefully arranged heaps of wood are covered with turf and earth and fired. A portion of the wood burns away, and the heat produced just chars the remainder.

Sugar and a number of other compounds, when gently heated, melt, and do not decompose until hotter than their melting-point.

Place a few grams only of ordinary white sugar in a retort as before, and heat slowly. After melting it will change colour, boil up and expand, giving off gases, which should be caught and examined
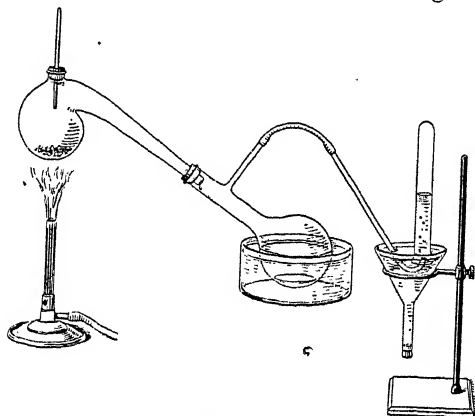
FIG. 27.

as before. It leaves a hard shining charcoal, which adheres to the glass. More tar will collect in the water than from the cotton or wood-shavings. Test the water with litmus.

OILS.—Five to ten cubic centimetres of olive or linseed, colza or other vegetable oil should be heated in a retort to which a condenser may be attached, as shown in Fig. 27.

The oils will commence to give off white fumes, which condense to some extent in the receiver, but much gas can be collected in the tube, and will be found to burn with a luminous flame. Unpleasant odours are produced by the escaping unburnt gases. A thin layer of closely adhering charcoal is usually left in the retort. It is small in amount. The oily substances collected in the receiver emit a sharp odour, and are otherwise different from the original oil. A "partial" decomposition has taken place. These oily substances are differently constituted to the cellulosic and woody materials or the sugars. The relative amounts of carbon, hydrogen, and oxygen also differ.

Petroleum, or Paraffin.—Petroleum, or paraffin oil, is a mixture of a number of compounds of carbon and hydrogen only.

Substances consisting of these elements alone are called *hydro-*

carbons. They are more difficult to decompose by simply heating than many other carbon compounds which contain oxygen or other elements in addition to hydrogen.

Petroleum may be considered to be a mineral, or of mineral origin.

FRACTIONAL DISTILLATION.—Many compounds of carbon may not only be melted, but boiled and completely converted into vapour without decomposition.

The "temperatures" at which a substance melts or boils are very characteristic and practically unalterable properties of the particular substance (see "Sulphur").

When a mixture of several substances, of differing boiling-points, is heated boiling will always commence before the temperature of the highest boiling constituent is reached, and often much below the calculated mean boiling temperature of the constituents.
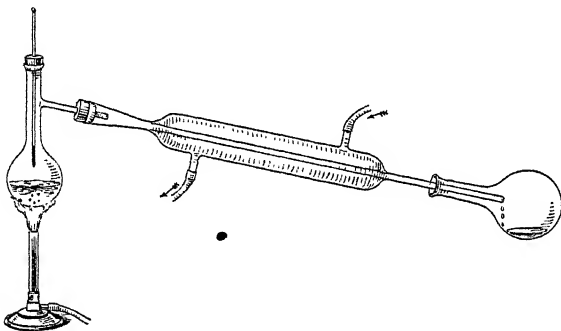
FIG. 28.

If two substances of widely differing boiling-points be mixed it is a comparatively easy matter to roughly separate them by distillation from an ordinary retort. The one of lower boiling-point will, on the mixture being heated, vapourise more rapidly, or to a greater extent, than the other. The portion vapourised or boiled off is never quite pure, as some of the higher boiling-point material also vapourises. The residue in the retort after a certain temperature has been reached may be a nearly pure substance.

For a simple distillation, to separate volatile from non-volatile substances, an ordinary retort or distillation flask, such as shown in Fig. 28, is quite sufficient.

Salt water or a "hard" well water should be distilled in an arrangement like Fig. 28, above. The boiling-point of a liquid may be ascertained in this apparatus. Whatever the liquid be, if pure, the temperature, as shown by a thermometer suspended *in the vapour* a little above the liquid, will not vary during the whole time of boiling or distilling over, provided that the vapour has free escape and the

barometric pressure is steady and some small pieces of rough wire or broken porcelain be in the retort.

When the quantity at disposal is very small the boiling-point may be ascertained by finding the temperature at which the vapour is exerting the same pressure as the atmosphere at the time. This is done as in Fig. 29, where the small bent tube contains a little mercury and a drop or two only of the liquid. As the temperature rises the vapour of the substance pushes the mercury down from the closed end, and when the columns are level the thermometer will be marking the boiling-point, as the pressure of the vapour is then equal to the atmospheric pressure on the open end of the tube.
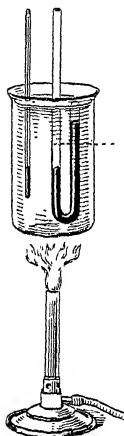
With complex mixtures, like ordinary petroleum, the constituents can only be separated by the use of a particular long head * to the retort or still, up which the vapours must ascend, and where they are cooled and condensed in a certain order.

Obtain a litre of ordinary lamp petroleum (paraffin oil). This has been, of course, distilled at the place of origin. It is, however, still a mixture.

The distilling flask should have a capacity of about 800 c.c., and be round-bottomed. (Copper is much preferable to glass.)

The dephlegmator tube † (Fig. 30) is fitted in with a cork, not with a rubber stopper. Such a flask should not have more than 500 c.c. of petroleum as a charge. On heating, many of the constituents of the mixture are converted into vapour, some in greater amount than others. These vapours ascend the tube. There is a certain amount of resistance due to the construction of the tube, and much cooling owing to the large surface. The flame must be arranged so that no serious " priming " of the tube occurs, and that two or three drops per second fall into the receiver at the end of the cooling tube. The action in the tall tube is roughly like this. Imagine three vapours, a, b, c, ascending the tube—a most volatile, c least. All are cooled, and some of each condensed. If the tube is long enough and the heating not too severe some of a alone will survive the cooling and enter the side outlet, whilst all of b and c and some a will be condensed and fall back. In condensing b and c also give up heat, some of which is expended on a. The thermometer will stand practically constant or rise only through a small number of degrees whilst any decided individual substance is distilling over. Sometimes it is only possible to collect "fractions" coming over whilst the thermometer is rising through 20 or so degrees. In such case these portions are again distilled. This may happen with the 500 c.c. of petroleum. Heat gently at first so that it slowly passes

FIG. 29.

* Dephlegmator.
† This may be quite straight, and can be easily made. 14 ins. by ½ in. (35 cm. by 1·5 cm.) is a convenient length and size. The theory of this process cannot be entered into here.

over, and catch in separate tubes or flasks the distillate at every 20° C. up to about 200° C. Measure each fraction. Allow the retort to cool, then measure the residue.

Place about 20 c.c. of the original oil in a small beaker. Pass a burning taper at the distance of about 1 cm. (or ½ inch) slowly over the surface of the oil. There will probably be no effect. Now do the same with the fractions obtained by distillation. The first fraction will probably have commenced to distil at about 100° C. Its vapour
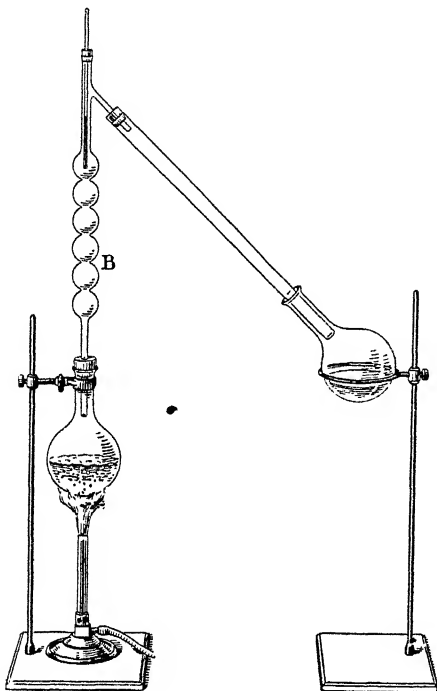
FIG. 30.

will probably "flash" or fire when the taper flame is passed over. Flashing is due to inflammable vapours being given off, which form explosive mixtures with air.

Most oils will give off sufficient vapour for this flash test at some particular temperature, and a special apparatus is generally employed for ascertaining this point. This is the "flash" point of the oil.

If some of this petroleum be "boiled away" in a test-tube a little black residue only will be left. If, however, the vapour of the oil be sent through a very hot tube charring takes place.

For this it is only necessary to heat some petroleum to boiling-point in a distilling flask and allow the vapour to pass through a narrow tube heated to full redness by a good Bunsen flame. A thin

layer of somewhat hard and glistening charcoal will be found lining the tube.

When any of these oils are burnt from a wick (or when a jet of their vapour is fired) and a cold object held in the flame so as to obstruct the air supply some charcoal is deposited, but its texture is loose; *it is "soot."* This material can be obtained from almost every kind of flame of a carbon compound by chilling or restricting air access, and when made in this manner is often called "lampblack."

Turpentine, camphor, resin, and many substances obtained from coal tar, such as benzene, naphthalene, &c., burn with very smoky or sooty flames.

Coal, when heated to a very high temperature, produces coke—a much denser and harder form of charcoal than given by ordinary plant products.

Pound up some ordinary coal. Half fill a small porcelain or platinum crucible with the fine powder, close with a lid, loosely, and heat as strongly as possible over a Bunsen flame, or, better, a large blowpipe flame. Much gas will be formed, and burn with a luminous and smoky flame. The heating should be continued until little or no more gas seems to be produced and the crucible is fairly red hot. After cooling the crucible will be found to contain a porous coke. It will appear to be one piece, and is much harder than wood charcoals. Heating for a long time to a very high temperature increases the hardness of the coke.

Gas carbon is formed in the retorts or clay tubes in which coal is heated in the manufacture of coal gas. It is produced by the decomposition of the gases, and is found on the upper parts of the retorts, where the temperature is very high.

Animal substances, as horn, bone, ivory, feathers, leather, wool, silk, &c., give, when heated, a peculiar carbon or charcoal residue. The gaseous products differ considerably from those produced with the previously mentioned substances.

Heat in a small retort or crucible (as with cotton—*ante*) either quill cuttings, horn shavings, or silk. Any of these will be observed to swell up and wriggle when first heated. Vapours escape which when tested with the litmus papers react quite differently from those from carbon or wood. The vapours have a very unpleasant odour. On heating to cessation of gas evolution the residual charcoal will appear as if fusion had taken place before final resolution. The charcoal is hard and shiny, and does not easily burn in air. Bone and ivory will give off similar volatile products, but the charcoal will retain the form of the original owing to the large quantity of mineral matter they contain. Animal products contain nitrogen, which is converted into ammonia at the temperature of charring.

All the varieties of charcoal or amorphous carbon mentioned will commence to burn in air when heated therein to some particular

degree. The more dense the charcoal the higher the ignition temperature. Graphites, diamond and gas carbons require not only a high temperature, but either pure oxygen or air containing some extra oxygen.

Some one of the charcoals made should be burnt either in pure oxygen or in air, so that the product may be caught and examined. About a gram, or less, of charcoal from cotton-wool or similar light substance may be ignited and dropped into a dry flask —say a litre flask—which is then quickly closed with cork or stopper and gently shaken so that the charcoal does not remain at one place. It will glow for a little time and then go out. Allow the flask to cool before opening. If done properly little difference of pressure will be noticed on opening. Some charcoal will be left, as there is little more than ·25 of a gram of oxygen available in the litre.

Different kinds of coke, graphite, and diamond may be tried in the same way as the charcoals. They will not continue burning in air.

A bottle (Fig. 31) should be filled with oxygen, and small pieces of coke, graphite, or diamond splinters wrapped in platinum wire (or foil), heated very strongly, and quickly immersed in the gas.

FIG. 31.

Assuming charcoal to be carbon, the action on burning may be represented by $C + O_2 = CO_2$, which means that 12 parts by weight of carbon have united with 32 parts of oxygen.

It should be noted that the oxygen is gaseous and the carbon a solid, the specific gravity of which may vary from about 1 to nearly 4. Whatever "allotropic" form the carbon may be in, the weight proportion remains constant. The carbon compound, called the dioxide, formed has the *same volume* as the oxygen before combination.

When charcoals are completely burnt the main product is the oxide called carbon dioxide or carbonic acid or carbonic anhydride. This compound is a heavier gas than air, and will remain for a little time in the bottle where made. After burning a charcoal in a bottle add about 20 c.c. cold water and shake up for a few minutes (filter, if necessary, or allow to settle). Add a few drops of litmus solution, or dip in a piece of blue litmus paper. The litmus will change to a *wine-red colour*, which indicates a feeble acid character.

To another bottle in which a charcoal has been burnt, either in air or oxygen, add about 20 c.c. *of lime or baryta water* (these are solutions of the hydroxides of the metals calcium and barium), and shake up. The liquid will become milky owing to a white *precipitate* of a compound of the oxide of carbon with the oxide of the metal.

The white precipitate is in each case a *carbonate* of the metal. Most metals can yield similar compounds. The two mentioned are
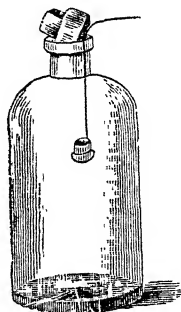
generally used as indicators or tests for this oxide of carbon, as they are white and insoluble in ordinary pure water.   Acids, as nitric or hydrochloric, decompose all these carbonates, the oxide of carbon (carbon dioxide) being generally visibly expelled, an *effervescence* taking place.

Chalk, marble, limestone, and other minerals are essentially calcium carbonate.

The composition of pure calcium carbonate is represented by $CaCO_3$, which means that in 100 parts by weight 40 are calcium, 12 carbon, and 48 oxygen.   The two former figures are the atomic
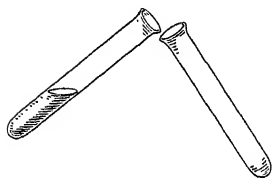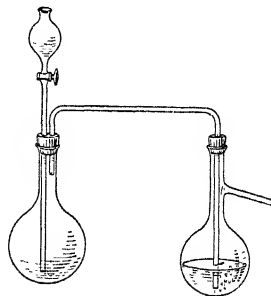
FIG. 32.   FIG. 33.

weights of the elements Ca and C, and 48 is evidently three times the atomic weight (16) of oxygen.

The lime or baryta water test is expressed by the equation

$$CO_2 + CaH_2O_2 = CaCO_3 + H_2O,$$
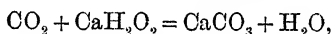
and the action of hydrochloric acid on the calcium carbonate by

$$2HCl + CaCO_3 = CaCl_2 + CO_2 + H_2O.$$
$$73 \qquad 100 \qquad 111 \quad 44 \quad 18$$
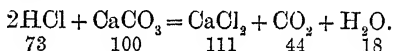
Calcium hydroxide solution becomes turbid or milky on shaking up with air, which contains about ·03 per cent. of carbon dioxide.

Place a few grams of chalk or marble in a test-tube and add two or three c.c. of hydrochloric acid.   Violent effervescence will take place, but without rise in temperature.

Collect some of the gas, by allowing it to flow over into some dry tubes (Fig. 32), and examine by litmus and by lime water.   The results should be the same as with the gas from the burning of charcoal.   A lighted taper or wood splinter will also be extinguished when introduced into the gas.

Potassium, or sodium, hydroxide solutions absorb carbon dioxide without any precipitation, the carbonates formed being very soluble in water.

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O.$$
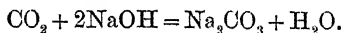
Carbon dioxide is most conveniently generated by allowing hydrochloric acid to drop on marble or chalk in a flask arranged as

in Fig. 33. The gas evolution is then under control. By passing the gas through water it is freed from hydrochloric acid, which is liable to be carried over.

In using an apparatus of this kind it is usual to allow the gas to escape for some time to expel air.

When all the air is expelled, complete absorption of the gas takes place when the exit tube of the apparatus is just dipped under the surface of a solution of sodium hydroxide. With this apparatus larger quantities of the gas may be obtained, and in a regular stream. The flame of most ordinary combustibles is extinguished by this gas, but several metals will burn in it.

Coil a few centimetres of magnesium ribbon and place at the bottom of a test-tube. Lead a stream of the carbon dioxide to the bottom
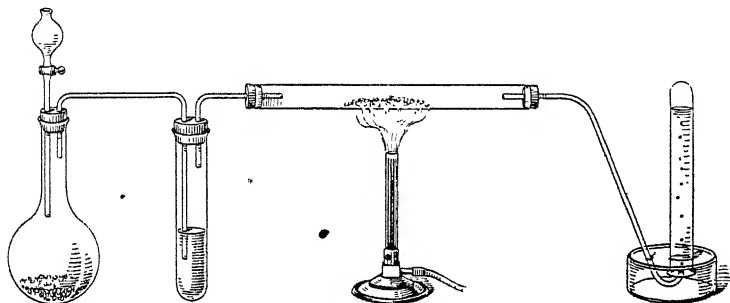
FIG. 34.

of the tube, and then heat strongly the place where the coil lies. Or the gas may be led into a flask and a piece of burning magnesium ribbon dropped in. The metal will not burn so well as in air. Black and white stains or splashes will appear on the glass. They are partly magnesium oxide, partly carbon. On adding a few drops of hydrochloric acid the white oxide will dissolve, leaving a black powder of carbon from the carbon dioxide. The action of the magnesium is shown in formulæ by $2Mg + CO_2 = 2MgO + C$. A few other metals will similarly decompose carbon dioxide.

CARBON MONOXIDE.—This compound consists of carbon and oxygen in the proportions by weight of 12 to 16 only. It can be produced by heating charcoal, or some metals, to a high temperature a gentle stream of carbon dioxide.

The carbon dioxide produced in the flask, from marble and hydrochloric acid, must be dried by passing through sulphuric acid instead of water, and then led over charcoal or galvanised iron wire, contained in a tube, which is heated as strongly as possible. The arrangement of the apparatus may be as Fig. 34 (or see " Steam ").

This gas is a trifle lighter, bulk for bulk, than air, and can be

collected over water, or potassium, or sodium hydroxide solution, in which it is not soluble, as carbon dioxide is.

The gas may be set fire to, and then burns in air with a blue flame. The product of its burning is carbon dioxide. Its production as described above is due to the abstraction of part of the oxygen from the carbon dioxide by the carbon, or the metal, under the particular conditions of temperature. $CO_2 + C = 2CO$ or $CO_2 + Zn = CO + ZnO$.

Another way of obtaining this oxide is to drop formic acid, or a formate as sodium formate, into strong warm sulphuric acid contained in a flask arranged as that for generating carbon dioxide from chalk (Fig. 33, *ante*). Perfectly pure carbon monoxide is evolved.

When carbon monoxide burns in oxygen or air the action may be represented by the expression $2CO + O_2 = 2CO_2$ (see later).

This oxide is produced in many technical operations on a very large scale, and is the chief constituent of most gaseous "fuels" or "heating" gases.

AVOGADRO'S LAW.—The formula employed to express water is based on the relative combining weights (16 parts of oxygen to 2 parts hydrogen) and volumes (2 of hydrogen to 1 of oxygen). The formula H_2O represents a *molecule* of water. Practically also it should be taken to mean 18 parts by weight of water. When the two constituents unite there is a condensation, two volumes of hydrogen and one of oxygen forming two only of steam or gaseous water.

Taking grams and cubic centimetres as weights and volumes, it becomes

Oxygen	.	.	.	16 grms. = 11,200 c.c.
Hydrogen	.	.	.	2 grms. = 22,400 c.c.
Steam	.	.	.	18 grms. = 22,400 c.c.

In the formation of carbon dioxide the volume or bulk of the carbon is apparently lost, the product of the burning of carbon having the same volume as the original oxygen.

Oxygen	.	.	32 grms. = 22,400 c.c.
Carbon	.	.	12 grms. = a volume, as a solid, of from about 4 to 5 c.c. in the case of diamond or graphite to nearly 12 c.c. with some forms of charcoal.

The formula CO_2 means, therefore, 44 parts by weight of this gas, and, if the parts are taken as grams, also a volume of 22,400 c.c. by volume at 0° C. and 760 mm. H_2O and CO_2 represent *molecules*. The weights of equal volumes of these substances as gases at the same temperature and pressure are as 18 to 44.

Almost all other gaseous substances show a like connection. That is, quantities represented by their simplest "weight formulæ" occupy the same volume. Thus:

Water (vapour)	.	.	.	.	H_2O	=	18 grms.
Carbon dioxide	.	.	.	.	CO_2	=	44 ,,
Carbon monoxide .	.	.	.	CO	=	28 ,,
Sulphur dioxide	.	.	.	.	SO_2	=	64 ,,
Ammonia	.	.	.	.	NH_3	=	17 ,,
Hydrochloric acid .	.	.	.	HCl	=	36·5 ,,
Methane	.	.	.	.	CH_4	=	16 ,,

All these various parts by weight occupy the same volume—viz., 22,400 c.c., if the weights be taken in grams.

This may be called the " normal volume."

These values seem to indicate that gaseous molecules may be all of the same size. Assuming 18 grms. of steam to represent a " molecule " in grams (it cannot be an atom, because it is divisible into two substances), then the above formulæ are also molecular, because they are the smallest formulæ applicable to these substances by weight and relative number of "atoms," and these weights all occupy under the same conditions of temperature and pressure the same volume. That is, these weights occupy the same volume as 18 parts of steam, and the steam itself occupies the same volume as its contained hydrogen, and experiment shows that 2 grms. of hydrogen occupy the same volume as the 18 of steam and also of the weights just given of the other gases. 2 may therefore be taken as the molecular weight of hydrogen. The above are compounds; the elementary substances oxygen, hydrogen, nitrogen, &c., evidently follow a similar law, since

$$H_2 = 2 \text{ grms.}$$
$$O_2 = 32 \quad ,,$$
$$N_2 = 28 \quad ,,$$
$$Cl_2 = 71 \quad ,,$$

This is arrived at experimentally by finding the *relative density* of the gases under similar conditions. (See " Vapour Density," later.)

Frequently air is taken as the unit of density of gases and vapours. The "molecular" weight of dry air may be for practical purposes taken as 28·8.

The density of any gas or vapour compared with air is given by dividing the molecular weight, if known, by 28·8. So that water vapour, $16 + 2 = 18$, and ammonia, $14 + 3 = 17$, are lighter and carbon dioxide, $12 + 16 + 16 = 44$, heavier than air.

Taken in conjunction with the metrical system of weights and measures, a chemical equation can be at once read in weight and in *volume of those products which happen to be gases.* For instance, in the production of carbon dioxide from chalk and an acid the equation as written gives weights :

$$CaCO_3 + 2HCl = CO_2 + H_2O + CaCl_2.$$
$$100 \qquad 73 \qquad 44 \quad 18 \qquad 111$$
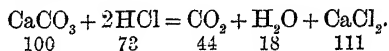
If these be assumed to be grams, the 44 of CO_2 occupy a volume of

22,400 c.c.   Supposing the chalk to have a specific gravity of 2, the 100 grms. would occupy 50 c.c.   The CO_2, on liberation from its union with the calcium oxide, CaO, assumes more than 400 times its volume in the combined state.   In the production of hydrogen from zinc and sulphuric acid, $Zn + H_2SO_4 = ZnSO_4 + H_2$, the

$$65 + \quad 98 \quad = \quad 161 \quad + 2 \text{ grms.}$$
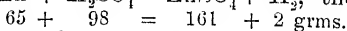
2 grms. of hydrogen $= 22,400$ c.c. and the 65 of zinc about 8 c.c., and the sulphuric acid from which the hydrogen comes about 54 c.c. The change in volume is therefore almost the same.

CHAPTER V.

SULPHUR.

SULPHUR is an elementary substance, and is found in some volcanic districts in a free state—that is, uncombined, as are nitrogen and oxygen in the atmosphere.

Enormous quantities exist in combination with some metals as sulphides and also as sulphates.

The element is a pale yellow solid, and can be obtained as " roll sulphur " or in irregular crystalline masses or in powder form, called " flowers of sulphur " or " flour of sulphur."

It is an exceedingly brittle substance which can be very easily powdered.

Heat a small quantity in a dry test-tube very slowly over a flame. It will melt into a pale yellow liquid, which does not wet the glass.

The solidifying-point temperature should be taken by stirring the melted sulphur with a thermometer until it sets. The temperature will be close upon 115° C. The melting-point can then be taken as indicated in Fig. 35.

Melting-point tubes are made by softening the middle of a small test-tube in the blowpipe flame and drawing out the glass to a long piece of fine tube of about 1 mm. diameter. Pieces of this about 3 cm. long have one end melted up. A *very small* piece of the solid is introduced (a piece the size of an ordinary pinhead is quite large enough), and the tube then attached, by means of a small india-rubber ring cut from a piece of ordinary rubber tubing by means of a sharp pair of scissors, close to the bulb of the thermometer. The liquid is slowly heated, and the temperature read off at the moment the substance melts.

The sulphur in the test-tube, on cooling down from its melting-point, will crystallise to a pale yellow confused mass clinging around the thermometer. Melt this sulphur again, and continue the heating after it is melted. It will become darker in colour as it

FIG. 35.

4

gets hotter, and at a certain temperature, which should be noted, it will become thick and viscid. Allow to cool again, remove the thermometer whilst the substance is fluid, and then heat again until it fairly boils in the tube. Vapour will be freely given off, which may take fire at the mouth of the tube. (The temperature is too high for an ordinary thermometer; it is 440° C.) Now pour out into cold water. The sudden chilling will cause the sulphur to assume a "modified" form (see "Ozone"). The chilled sulphur can be stretched and extended almost like india-rubber. It is one of several "allotropic" forms into which sulphur easily passes under certain physical treatment. This form is, unfortunately, not permanent, but gradually reassumes the brittle character.

Sulphur is quite insoluble in water. This can be proved by boiling a few grams in water, drying, and weighing again. Some other liquids, especially some oils, dissolve sulphur—notably turpentine and carbon bisulphide (the latter is a very poisonous substance). Boil a small piece of sulphur in about 10 c.c. of turpentine ; pour into a dish. On cooling crystals will form.

Melt about 200 grms. sulphur in a dish. Allow to cool until a crust just forms on the surface. Break two holes through the crust and pour the liquid part out carefully. The cavity will be found full of crystals. From a chemical point of view, sulphur in many respects resembles oxygen. This is especially the case as regards the ease with which it combines with metals.

Silver, which will not rust or unite with oxygen under any ordinary circumstances, will burn quite well in sulphur vapour. Heat a small piece of silver in a test-tube or a small porcelain crucible as strongly as possible, and then drop in a *smaller* piece of sulphur. The sulphur will vapourise almost immediately, and the metal will then burn or glow, forming a sulphide, which melts by the heat of the reaction.

Perform a similar experiment with the metals copper, mercury, and lead. The action will be found to be almost as energetic as with silver. Zinc and aluminium can scarcely be heated to a sufficiently high temperature in a test-tube to start the action, but at a very high temperature they also combine with sulphur.

A strong solution of sodium hydroxide or a mixture of slaked lime and water (calcium hydroxide), when heated with powdered sulphur, form yellow solutions which contain some sulphides of those metals.

All these compounds are sulphides. As a rule, they are crystalline and generally brittle solids, and quite unlike either sulphur or the metal. Some of them are quite easily attacked by acids, and they all change when heated in contact with air.

The result of the acid attack on the sulphides is generally the formation of sulphuretted hydrogen, or hydrogen sulphide, as one product.

This is analogous to the action of acids on metallic oxides, where water is one product. The actions can be shown, and compared, by symbols thus: $CuO + H_2SO_4 = H_2O + CuSO_4$; $FeS + H_2SO_4 = H_2S$

+ FeSO$_4$, &c. Hydrogen sulphide happens to be a gas at ordinary temperatures, whilst hydrogen oxide is a liquid. Otherwise there are many analogies between the two.

Sulphur burns when heated in air to some temperature above its melting-point. When *very* carefully heated it may be evaporated without taking fire. The flame of sulphur in air is pale blue, and white smoke is generally formed. In oxygen the flame is more violet than blue.

A piece of moistened blue litmus paper held over the flame will become reddened. The choking fume given off is an oxide of sulphur. This oxide consists of equal weights of sulphur and oxygen. It is the main product of the burning of sulphur either in air or oyxgen. It is known as sulphur dioxide (SO$_2$). It has the same volume as the oxygen or air employed in its formation.

Place several small pieces of sulphur in a small dry flask with cork and tube (Fig. 36). The tube should dip two or three centimetres
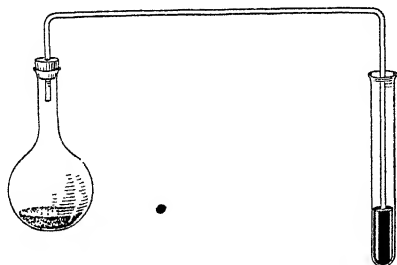
FIG. 36.

under mercury. Bring a red-hot wire in contact with the sulphur to ignite it, and quickly replace the cork and tube. The pressure of mercury must be enough to prevent escape of gas during the burning. After cooling down the mercury will rise but a centimetre or so above the level in the cup, showing, roughly, that the volume is not altered.

Sulphur dioxide sufficiently good for the following experiments can be made by burning some sulphur in a large flask full of oxygen (or even air). Cover the bottom of a flask with coarse sand, fill with oxygen gas, cover the mouth with a watch glass. Now melt and set fire to a few grams of sulphur in a small dish, and pour some of the burning sulphur into the flask and again close with the watch glass. The flame will be brighter in oxygen than in air. It will finally die out. After standing for a short time the fumes of vaporised sulphur will settle. The sulphur dioxide is a much heavier gas than air, and can be poured out or decanted into several test-tubes, and each then treated as follows:

I. Introduce a strip of moistened blue litmus paper. It will be reddened.

II. A burning taper will be extinguished, and the gas itself will not inflame.

III. A piece of burning magnesium ribbon will continue to burn, and some sulphur *may* be liberated.

IV. A few drops of potassium permanganate solution on a rod or a piece of paper coloured by the same will be decolourised by the gas.

V. Invert a tube of the gas in a basin of cold water. The gas will dissolve and water rise in the tube. This water will redden blue litmus. It is sulphurous acid, H_2SO_3, produced by the union of the gas with water.

VI. Drop a very small quantity of red-lead into a tube of the gas and warm gently. It will be changed into a white substance— lead sulphate, $PbSO_4$.

Sulphur dioxide oxidises somewhat easily either in solution in water or as a gas in a moist state. The end result of its oxidation is sulphuric acid or a sulphate, but the next stage of oxidation may be obtained by heating the sulphur dioxide with oxygen gas.

VII. Make a little coil of platinum or iron wire red hot and hold in the open end of a tube or flask containing sulphur dioxide. White fumes will form at the junction of air and the gas. These fumes are SO_3—sulphur trioxide. They will absorb and combine with the atmospheric moisture, forming sulphuric acid, H_2SO_4. Put *one* drop of water on a strip of white paper and hold in the fumes. Then dry the paper carefully. It will char, or become black, where it was moistened.

The platinum or iron in the above experiment are called catalytic or contact agents. SO_2 combines very slowly with oxygen under ordinary temperature conditions. The presence of some materials assists this combination, whilst not themselves undergoing alteration.

SO_3 is a crystalline, volatile solid which combines very energetically with water, producing much heat in the process.

FORMATION OF A SULPHATE.—Melt a few grams of potassium nitrate (nitre) in a porcelain dish and add small pieces of sulphur. A violent combustion will take place. Nitrogen and some red fumes of oxides of nitrogen will be given off, and, if too much sulphur be not used, the greater part of the product will be potassium sulphate. When cold the melted mass should be dissolved in the least possible quantity of boiling water. On cooling, this solution will give crystals of the sulphate.

Metallic sulphides may be similarly oxidised by melted nitre. One product will be potassium sulphate, and the other, *in most cases*, an oxide of the metal. Pound up a few grams of copper, iron, or lead sulphide, and fuse with nitre in a dish as above. After cooling wash out, as before with hot water. The liquid will require filtering, and on the filter paper will be found an oxide of the metal. If minerals are used they must be finely powdered, and not more than one or two grams taken to about five or six of nitre.

SULPHURIC ACID can easily be made on the small scale. Technically, two processes are in use. In one nitric acid or oxides of nitrogen are the oxidising agents, converting SO_2 in the presence of

air and water into the acid. In the other SO_2 is made to combine with atmospheric oxygen by the influence of a contact material, either platinum or some forms of iron oxide or silicate.

A very small quantity—1 or 2 c.c.—of sulphuric acid may be made by filling, say, a litre flask with SO_2 and then adding about 2 c.c. of very strong nitric acid. The flask may be covered with a watch glass and left some hours. The fumes and coloured gases will slowly disappear, and the flask may then be washed out with a few c.c. *only* of water, which is then carefully boiled down in a small flask until white fumes begin to come off. On cooling, a few drops of oily liquid—sulphuric acid—will be left.

Sulphuric Acid by Electrolysis of a Sulphate.

Make in a dish or beaker a strong solution of copper sulphate in warm water. Place in this strips of platinum foil or rods or plates of battery or gas carbon to act as electrodes, and lead in a current from two or three storage cells. Metallic copper will be deposited on one plate and oxygen given off at the other. The liquid will finally become colourless. Pour off the clear liquid, and evaporate, as in the previous experiment, in a flask or dish. Other methods are to oxidise SO_2 by the action of bromine or iodine and water. Bromine or iodine are placed under water in a large flask and SO_2 gas passed in. The reaction $SO_2 + Br_2 + 2OH_2 = 2HBr + H_2SO_4$ takes place. On heating, the HBr is driven off and the acid in solution can be concentrated by evaporation. The process *must* be conducted under a draught arrangement. Weak solutions of sulphuric acid on evaporating or boiling down lose water and leave a strong acid.

CHAPTER VI.

QUANTITATIVE EXERCISES.

IN a previous chapter (Chapter III.) atomic and combining weights
have been spoken of in connection with hydrogen and water.

Some of the following experiments should be performed as early
as possible after the introductory chapter.

Relative Combining Weights, and Formulæ from Percentage Composition.

Atomic and combining weights of the elements are in some
cases identical values, as, for instance, with chlorine and hydrogen.
With oxygen and hydrogen the atomic weights are as 16 to 1, and
the combining or equivalent weights as 8 to 1. Few metallic sub-
stances combine directly with hydrogen, whilst many combine most
readily with oxygen or sulphur, or chlorine, or iodine, and these in
turn combine easily with hydrogen, so that indirectly the combining
weights may be obtained as compared to H as unity.

As easy practical examples, the combinations of copper, silver,
lead, and iron with oxygen or sulphur or halogens may be first taken.

Metals and Oxygen, Sulphur or Chlorine.

LEAD AND OXYGEN.—Clean, dry, and bend a piece of hard glass
tube to the form of Fig. 37,* and then weigh it. Insert a small piece
of pure lead—1 to 2 grms. is *quite* enough—weigh again, support
the tube conveniently, and heat until the lead melts in the bend.
The natural draught of air through the tube will eventually oxidise
the metal, but it is better to blow, very gently, a stream of oxygen
from an oxygen cylinder, or any source, just into the short end of
the tube. The lead will glow and burn, and if the admission of
oxygen be not regulated the oxide of lead, in forming, will become
very hot and melt through the glass. The lead oxide formed is
quite transparent when fluid, so that it is easily seen when all the

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* This form of tube serves to heat up a weighed amount of some metallic
sulphide, as PbS or Ag$_2$S, which is then heated in the slow current of air
caused in the tube by natural draught. In this case a certain amount of
sulphate is produced. The experiment should be done with silver sulphide,
which forms almost the theoretical amount of sulphate, and with lead sul-
phide, which scarcely forms half the theoretical.

metal has been combined. The tube should be cooled slowly by laying it on some asbestos wool.

Example (actual).

Tube	19·5768 } ·3412 metal.
„ + lead	19·9180 }
After oxidation	19·9444 } ·3676
	19·5768 }

·3412 grm. of lead has therefore taken up ·0264 grm. of oxygen in forming an oxide, which contains $\frac{0264 \times 100}{·3676} = 7·18$ per cent. of oxygen and 92·82 per cent. lead.
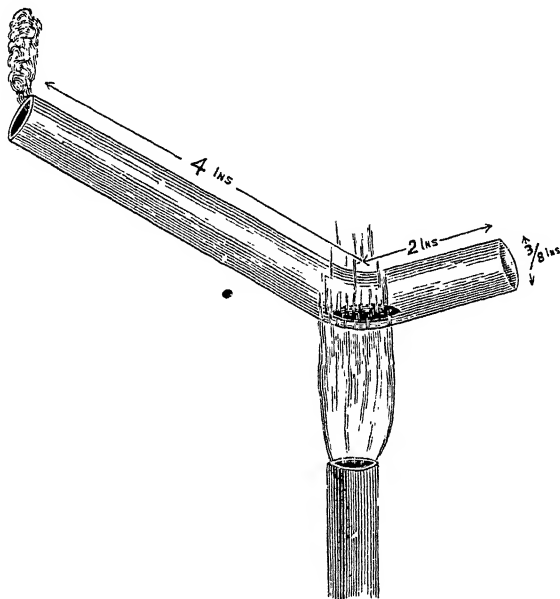
Fig. 37.

Dividing the percentages found of each element by the respective atomic weights, $\frac{7·18}{16} = ·448, \frac{92·82}{207} = ·447$: these figures are practically as 1 to 1. Or, in another way, the amount of oxygen, ·0264, taken up by the ·3412 of lead is in the proportion of 15·8 to 205 (nearly).

The combining weight of lead, according to the standard of oxygen being 16, is therefore about 206. (The most recently obtained values are given in Table I., and the ordinarily used value is 207.)

SILVER AND SULPHUR.—Clean and weigh a small porcelain crucible, with its lid. Place a small piece of silver, in thin sheet or

foil, in the crucible and weigh again. The quantity need not exceed 2 grms. and may be as little as ·2 grm.

Place the crucible with silver on a pipe-stem triangle on a tripod and heat with a clear Bunsen flame nearly to redness. Lift the lid and drop in a small piece of clean roll sulphur and replace lid. There is no object in weighing the sulphur—the quantity used must be a little more than the silver taken. As the two combine the temperature inside the crucible will be seen to rise. The materials will glow. Sulphur vapour will escape and burn around the edges of the lid. Continue the heating until these fumes cease. Lift the lid and repeat the treatment with sulphur. Finally cool and weigh. There should be an increase in weight. The lid must be kept on until the crucible is quite cold to prevent access of air. The product will be a black, crystalline mass.

Example.

Porcelain crucible   .   . 15·4060 ⎫
      ,,   ,,   + Ag   . 16·0560 ⎬ 0·6500 silver.
After heating with sulphur . 16·1522 ⎫
                     15·4066 ⎬ 0·7462 silver sulphide.

The silver-sulphur compound formed contains, therefore, ·7462 − ·6500 = ·0962 sulphur, or 12·88 per cent., and silver 87·12.

Now if the percentages so found be each divided by the respective atomic weights, viz.,

$$\frac{\text{S per cent. } 12\text{·}88}{32} = \text{·4 or } 1$$

$$\frac{\text{Ag per cent. } 87\text{·}12}{108} = \text{·8 or } 2$$

These are evidently the relative number of atoms of the substances in the compound, and it is for this reason sulphide of silver is formulated as Ag_2S. (See "Atomic Weights.")

COPPER AND SULPHUR.

COPPER AND SULPHUR.—This operation is somewhat less easy than the former. The temperature must be higher, and air more carefully excluded during the cooling. Otherwise the procedure is the same. Two compounds of sulphur and copper are known. Of these one contains exactly half the quantity of sulphur or double the quantity of copper compared with the other. The one with the lower quantity of sulphur withstands the higher temperature. It is formulated as Cu_2S. It is a crystalline, blue substance.

LEAD AND SULPHUR.

LEAD AND SULPHUR.—A similar experiment with lead is still more difficult. A much higher temperature must be maintained for a little time, the crucible with lead and sulphur being heated in a good blowpipe flame for twenty or thirty minutes and cooled very carefully with exclusion of air.

Example.

Crucible	.	.	.	.	23·4510) 1·353
„ + lead	.	.	.	.	24·8040)
After heating + sulphur		.	.	25·0220) 1·571
				23·4510)

The lead sulphide formed contains 13·87 per cent. of sulphur, and therefore 86·13 of lead.

$$S = \frac{13·87}{32} = ·433$$

$$Pb = \frac{86·13}{206·4} = ·417$$

—nearly 1 : 1, as represented by PbS.

Other metals—for instance, tin—may be tried in a similar manner, when it will be found that each requires some particular care as to temperature, to avoid loss by vaporisation, &c.

The elements chlorine (bromine), iodine easily form compounds with metals, and as a rule compounds of a relatively simple type not readily decomposed on contact with air or water. They are consequently well adapted for experiments on combining weights.

Example.

SILVER AND IODINE OR CHLORINE. *Iodine.*—Weigh as

before in a porcelain crucible about ·2 to ·5 grm. pure silver. Heat strongly over a clear Bunsen flame; then drop in a few crystals of iodine, quickly covering the crucible with the lid. The silver will glow and the product melt into a brown liquid. The temperature must be kept up for a little time and several additions of iodine made. The melted iodide in the crucible will be seen to pale considerably as it cools, and when solid and cold is a pale yellow crystalline substance. Air has no effect on the compound even at a red heat.

The experiment requires a little care. The silver should be in thin pieces or fine wire, and the temperature as high as the Bunsen flame will make it before the iodine is added.

Iodine is very volatile, and the excess very readily passes away.

Using the (rounded) atomic weights, it may be stated that the silver and iodine in this compound are to each other as 108 to 127, or atom to atom, as represented by the formula AgI.

Chlorine.—This operation, on account of the gaseous and disagreeable character of the chlorine, requires a little more elaboration.

A hard glass tube of 1 cm. diameter and 10 cm. (or 4 ins.) long is cleaned, dried, and weighed, and the silver, in thin pieces or wire, placed about the middle and the tube and metal again weighed. The tube is then supported, and the part around the metal strongly heated.

Chlorine gas is then generated in a flask, such as a distillation flask with a side tube, from a few grams of potassium permanganate and strong hydrochloric acid, and allowed to pass over the silver until

the whole melts down to a clear liquid, no more metal being visible. It is then cooled and weighed again. The actual operation takes but a few minutes if the stream of chlorine is moderately strong, but some arrangement must be made to absorb or remove the excess of chlorine unless the experiment be done under a well-ventilated fume closet. The form of tube used for oxidising lead (Fig. 37) will also answer to hold the metal.

This experiment may also be performed in a porcelain crucible if there be a good supply of chlorine, the lid of the crucible being slightly lifted to allow the tube leading the chlorine to enter whilst the crucible is being strongly heated.

Examples of Interaction or Interchange, or Equivalent Replacement.

Many of the chemical actions and processes connected with manufactures, &c., are of this type—that is, elementary substances acting on a compound or compounds undergoing interchange or redistribution of elements.

Silver forms a nitrate of the composition $AgNO_3$. This on contact with a chloride gives a chloride of silver as one product, which on account of its stability may be easily isolated or retained and the other products removed. For instance, silver nitrate and ammonium chloride when heated together give silver chloride, a stable substance under a wide range of temperature, and ammonium nitrate, which easily undergoes internal change and resolution into simpler substances, such as water and nitrogen.

In aqueous solution the change expressed by $AgNO_3 + NH_4Cl = AgCl + NH_4NO_3$ takes place, but when they are heated together all excepting the silver chloride is volatilised.

Weigh a porcelain crucible alone and then with a few crystals of silver nitrate. Cover these crystals with about twice their bulk of ammonium chloride. Heat the crucible, at first gently and then more strongly, over a Bunsen flame until all fumes cease to appear and the product has melted into a clear mass.

Example (actual).

Crucible	.	.	.	.	.	18·0600 } ·6172 $AgNO_3$
„ + silver nitrate	.	.	18·6772			
After heating with ammonium chloride	18·5765 } ·5165 $AgCl$					
	18·0600					

The change from silver nitrate = 170 to silver chloride 143·5 demands ·5232 chloride from ·6172 silver nitrate, so that in this experiment the difference is ·0067, or about ·1 per cent. loss.

This kind of action takes place in many other cases besides the one here mentioned. The student should prepare some metallic nitrates by the action of nitric acid on the metal or oxide, and then convert a weighed quantity into the chloride by heating with ammonium chloride (which reacts in most cases). Where the chloride is very volatile the method is inapplicable.

Calcium or lead or copper will give good results, and moderate temperatures only are required.

Most nitrates also decompose and leave oxides on heating. Several nitrates, as those of lead, copper, should be made, and weighed quantities heated to redness and the resulting oxides weighed.

An easy exercise on the equivalence between oxygen and chlorine or chlorine and sulphuric acid is to weigh a few grams of copper, dissolve in dilute nitric acid, evaporate the solution to dryness, and ignite carefully. The oxide CuO is left. After weighing, the oxide is dissolved in strong hydrochloric acid, which in turn is evaporated carefully to complete dryness and again weighed. This will give the equivalence of Cl_2 to O. The chloride is now moistened with a little strong sulphuric acid, and again evaporated until all fume of hydrochloric and sulphuric acids ceases. The substance will now be the dry copper sulphate $CuSO_4$. It should be nearly white. The copper chloride may also be converted into sulphate by heating with ammonium sulphate, but the operation requires considerable care.

Examples of Expulsion of an Element or Group of Elements.

Many crystalline salts contain water. This water is in many cases expelled by heating the salt to or a little above the boiling-point of water. Sometimes a red heat is necessary to expel the whole of the water. This high temperature can, however, only be applied in some cases where no further decomposition takes place excepting the crystal water. As an example of this, sodium phosphate, or borax $(B_4O_7Na_2 + 12H_2O)$, or sodium sulphate may be taken. Weigh about ·5 to 2·0 grms. of the salt in a small dish or crucible, heat for some time in a hot-air oven, and finally over the blowpipe to complete fusion. Care must be taken during the heating that the substance does not spirt. The first part of the drying should always be done in the hot-water or steam oven. The dish and substance is finally placed in a desiccator to cool before weighing. The heating must be repeated until the weight becomes constant.

It will be found an advantage if the student prepares for himself a number of salts with water of crystallisation—or constitution, as it is termed in some cases—and determines this water by heating up to different temperatures in an air bath.

Copper sulphate may be made by dissolving the oxide in hot dilute sulphuric acid, or the metal in strong hot acid—in the latter case taking equal weights of copper and acid in a flask of about half a litre capacity, the copper being in turnings or thin pieces.

Fumes of sulphur dioxide and sulphuric acid are evolved, so that a draught closet is necessary.

The reaction may be expressed
$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$
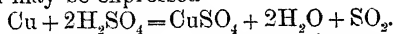
A powder of indeterminate colour will form as the metal dissolves. After *completely cooling* water is to be added and the contents of the flask heated to boiling, filtered, and whilst cooling be stirred so that small crystals form. These are to be pump-filtered off and

recrystallised in a similar manner.   The crystals are then drained and dried by pressing, *not rubbing*, between clean filter paper.

Purchased copper sulphate, or any other salt, should be purified in a similar manner by recrystallisation.

As traces of iron are not so easy to get rid of, the process of solution and crystallising should be repeated at least three times, commencing with 40 or 50 grms. of the pure commercial salt.   When pressing between filter papers *do not rub*.   The crystals must be obtained dry by this means only.   They are liable to lose some crystal water on exposure in a warm place, and must *not* be placed in a desiccator.

Example.

Crystallised copper sulphate.

Crucible	15·4775	} 3·3904
,, + salt	18·8679	}
After heating one hour at 100° C.	17·8879	} 0·9800
= 28·90 per cent. loss.		0·2482
Again heated to about 240° .	17·6397	

= 7·32 per cent. loss.

Total loss = 36·22 per cent.

Calculated for $CuSO_4$, $5H_2O$.   Crystal water = 36·14 per cent. (See later.)

Nitrates, chlorates, carbonates, and other salts, when heated alone to a moderately high temperature, undergo decomposition of a more or less complex nature.   In some cases it is within certain ranges of temperature, quite sharp and definite, admitting of employment as an exercise.

POTASSIUM CHLORATE when moderately highly heated loses all its oxygen, becoming KCl.

As a quantitative experiment this can be performed in a weighed test-tube if only a small quantity of the salt be taken, say ·2 to ·5 grm.   Weigh the clean dry test-tube, introduce the dry salt in fine powder, weigh again.   Then heat very gently until the whole of the salt is melted ; keep melted for some time, very gradually increasing the temperature-so that the oxygen does not come off too rapidly. The tube is best inclined, or a watch glass placed with convex side down, on the tube.   With a little care there will be no loss from spirting.   Weigh immediately after cooling in a desiccator, as the KCl absorbs moisture somewhat rapidly.   A little tuft of asbestos wool placed in the middle of the test-tube, and weighed as part of the tube before putting in the salt, will effectually stop loss by the spirting of salt.

CALCIUM CARBONATE ($CaCO_3$).—Weigh out in a platinum or porcelain crucible about .5 to 1·0 grm. pure Iceland or calc spar. Heat over the blowpipe as strongly as possible for thirty minutes.

Cool, and weigh again. Repeat the heating and weighing until a constant weight is obtained.

The loss in weight should be close upon 44 per cent. For $CaCO_3 = CaO + CO_2$.

$$\underset{100}{} \quad \underset{56}{} \quad \underset{44}{}$$

A little pure cane sugar, which need not be weighed, placed in the crucible, assists in liberation of the CO_2. The crucible must, however, be left partly open, to burn off any carbon from the sugar.

Many other carbonates, as those of copper, lead, manganese, &c., easily lose carbon dioxide when heated.

Alkali carbonates heated alone do not give off the whole of the CO_2, but when heated with acids, or acid salts, the CO_2 is expelled.

SODIUM OR POTASSIUM CARBONATE, and an acid salt.—

Weigh about ·5 grm. of dried sodium carbonate into a moderate sized crucible. Cover it with at least five times as much potassium dichromate that has been melted and then pounded up finely. Weigh again. The difference gives amount of sodium carbonate and potassium dichromate. Now heat gently over a Bunsen burner until the whole is in quiet fusion. Continue the heating for fully twenty minutes; cool and weigh. Heat again for a few minutes *carefully* over the blowpipe. The weight should be constant.

The reaction taking place, if the temperature has not been too high, is—

$$K_2Cr_2O_7 + Na_2CO_3 = CO_2 + \begin{cases} Na_2CrO_4 \\ K_2CrO_4. \end{cases}$$
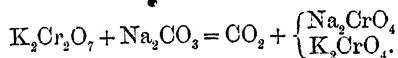
Silica, SiO_2, may be used for this experiment, instead of dichromate, if it can be obtained in a fine powder.

The process is then similar—viz., weigh the crucible and SiO_2 taking a considerable excess of SiO_2. Then add and weigh about ·5 grm. of the carbonate. Mix carefully by means of a platinum wire in the crucible, place on the lid and heat, gently at first, finally over the blowpipe flame as high as possible for twenty minutes. The loss of weight should be CO_2 only, according to the equation : $K_2CO_3 + SiO_2 = K_2SiO_3 + CO_2$. A gas-heated muffle is somewhat better for many of these experiments than a blowpipe flame.

Nitrates when heated alone are either decomposed into oxides of nitrogen and a metallic oxide or in some cases free nitrogen and oxygen are given off. When heated with sulphuric acid sulphates are formed, and with silica silicates.

The alkali nitrates are easily decomposed by heating with silica. Weigh out in a crucible about 5 grms. of fine sand (as with the carbonates), then mix with this, by means of a wire, about ·5 grm. of potassium nitrate; weigh, and then heat in the covered crucible very carefully to redness. Keep red hot for fifteen or twenty minutes, and then heat a little stronger over the blowpipe for a few minutes only.

$$4(KNO_3) + 2SiO_2 = 2K_2SiO_3 + 2N_2 + 5O_2.$$
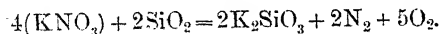
Example (actual).

Potassium nitrate and silica.

Crucible and sand, SiO_2	.	.	.	31·4362
„ + KNO_3	.	.	.	32·3534
Nitrate taken	.	.	.	.	0·9172
Weight after heating	.	31·8615
Loss	.	.	.	.	·4919

Loss per cent. $= 53·52 =$ all the nitrogen and five-sixths of the oxygen.

According to the equation $4(KNO_3) + 2SiO_2 = K_2SiO_3 + 2N_2 + 5O_2$, the loss in weight should be 53·40 per cent.

Nitrates, carbonates, haloid salts, &c., are all easily decomposed by strong hot sulphuric acid, and as sulphates are, as a rule, very
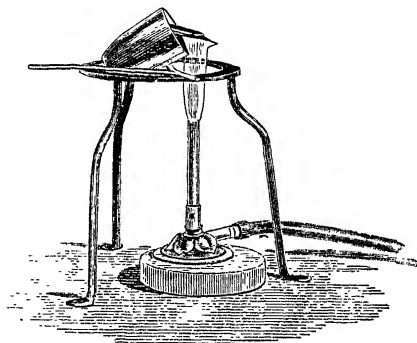
FIG. 38.

stable against a high temperature, many examples of displacement may be studied. They require, however, somewhat more care with sulphuric acid than with SiO_2 and similar non-volatile agents.

CHLORINE in common salt, **IODINE** in potassium iodide, or N_2O_5 in nitre, can all be expelled by heating with strong H_2SO_4 in slight excess. Similarly with a large number of salts of other metals. A platinum crucible is most convenient for this, but with care it may be performed equally well in an ordinary porcelain one. Weigh a crucible, place in it a small quantity of the salt, and weigh again. If the quantity taken is more than 1 grm. throw some out; if under ·5 a little more may be taken. After one or two trials the amount taken will approximate to 1 grm. Arrange the crucible on a triangle as in Fig. 38, and wedge the lid edgewise in the opening. Drop gently not more than ten drops of concentrated sulphuric acid into the crucible, wait until the effervescence has almost ceased, then place a very small flame under the protruding part of lid, so that a draught of heated gases flows over the contents of the crucible. The evaporation of the excess of sulphuric and of the volatile acid liberated

takes place gradually and without spirting. When the contents of the crucible appear quite dry turn up a larger flame, and finally heat quickly to redness. •It is generally necessary and always advisable to add an additional quantity of the acid and treat as before, in order to be sure that all is converted into the sulphate.

This action of sulphuric acid can be studied in connection with—

AN INVESTIGATION OF COMMON SALT.—Ordinary common salt is not quite pure. It is soluble in cold water, and slightly more so in boiling water.

Dissolve as much salt as possible in about a litre of boiling water. Filter the liquid whilst boiling hot, cool rapidly by immersing the beaker in cold water, and stir vigorously so that the crystals formed will be small. They then can be filtered off, preferably on a pump filter, and most of the impurities remaining in solution can be drained off. (It is somewhat better to add a little concentrated hydrochloric acid to the hot salt solution or lead in gaseous hydrochloric acid. More salt will then crystallise out, and ordinary impurities are better held in solution.)

The salt crystals may be dried and then melted by heating, in a crucible, either over a good Bunsen flame or in an ordinary fire. The substance crystallises as it sets and slowly falls in pieces in cooling. If melted and poured into a mould an idea of the change of volume on solidification may be obtained.

The specific gravity of a saturated solution of the purified salt should be taken at some definite temperature, say 15° C., and compared with pure water at the same temperature. The saturated solution is easiest made by allowing a considerable quantity of salt to stand, with less than sufficient water to dissolve it, over night, or shake it frequently during a few hours. A Sprengel tube is most convenient for the sp. gr. determination, but the usual sp. gr. bottle may be employed ; also a few (20 or 50) cubic centimetres may be measured out into a weighed flask and the weight compared with that of the same volume of water at the same temperature.

A small quantity (see above) of the fused salt should be weighed for treatment with sulphuric acid.

The substance finally left in the crucible is sodium sulphate, and the values obtained should agree substantially with the equation $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$; that is, the amount of salt taken and the amount of sodium sulphate obtained should be as 117 to 142. Retain this for further investigation.

A larger quantity of salt may then be used for the formation of hydrochloric acid gas (see later). The residue is sodium hydrogen sulphate—an acid salt. It dissolves in boiling water pretty freely, and on cooling and stirring the solution crystals consisting of $NaHSO_4$ are obtained. The reaction at the temperatures employable in glass vessels is $NaCl + H_2SO_4 = NaHSO_4 + HCl$.

Chlorine in Salt by Precipitation with Silver Nitrate.

Place a few grams of the pure salt in a small tube or weighing bottle. Weigh this, then shake out carefully not more than ·5 grm.

into a beaker and weigh the bottle again. Dissolve the weighed salt in about 25 c.c. hot water with 1 c.c. of dilute nitric acid; heat until boiling, and add slowly a solution of silver nitrate until the white precipitate ceases to form. Then add a couple of c.c. more silver nitrate solution. (This addition is known as an " excess," and is to make quite sure that the reaction is completed.)

Keep warm, but not exactly boiling, for a few minutes, during
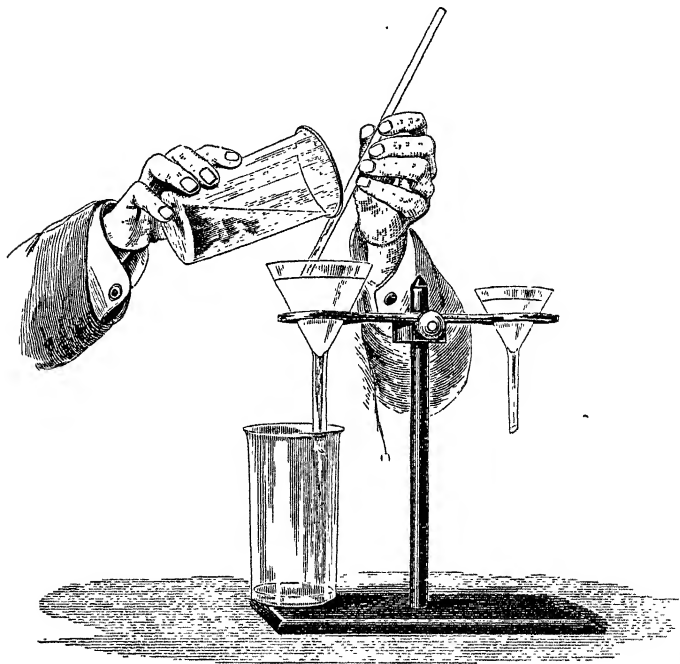
Fig. 39.

which a filter paper (either plain or folded) is got ready—viz., placed in the funnel and wetted with hot water.

The folded or plaited filter papers may be employed for this work, as with care they filter more rapidly than the ordinary method of folding and with equal certainty of securing the whole of the precipitate on the paper. The paper must sit well within the glass funnel.

The precipitate settles rapidly. Pour off the liquid above the precipitate into the filter. To do this properly and safely, because ALL must go through, requires that the liquid should be poured from the beaker down a glass rod, which should be held in the left-hand with one end over and well towards but not touching the centre of the paper funnel or cone, and inclined at an angle (see Fig. 39).

Every visible particle of the precipitate must be detached from the beaker and washed by a fine jet of water, from the "wash-bottle," into the filter. The precipitate must then be washed by pouring hot water five or six times over the precipitate and allowing to drain away between each addition. It is scarcely necessary to say that the filtrates must in all cases be *absolutely crystal clear* and all the precipitate be retained by the paper.

The test for complete washing is when a few drops of the wash-water give no appreciable residue when evaporated on a piece of glass, or a porcelain dish.

The precipitate may now be dried by placing the glass funnel and filter in a drying oven, or in a dry clean place if time be no object.

Some precipitates do not need to be dried in the paper, but may be heated up or burnt with the filter paper (see later), where this treatment has no decomposing effect.

The drying can sometimes be much facilitated by a final washing with warm methylated spirit. If the washing has been complete, the precipitate will detach almost completely from the paper when dry. Weigh a *porcelain* crucible during the drying of the precipitate. Spread a piece of clean writing-paper; on this place the weighed crucible; detach, by gently rubbing the paper together, the precipitate from the paper, dropping it into the crucible. Sweep any particles falling on the writing-paper into the crucible with a small dry camel's-hair brush, or a quill feather. This needs care, and nothing else should be thought about whilst doing it; as *all* the particles from the paper must come into the crucible.

The paper, from which nearly all the precipitate has been removed, must now be burnt in such manner that all the ash and any adhering precipitate are collected. Have the paper folded so as to form a semicircle, and double, of course. Then fold up into a strip about a centimetre, or $\frac{1}{2}$ inch, wide. Now start at one end, and roll up tightly into a coil, and around this wind several folds of platinum wire.

Hold over the crucible, or, better, invert the lid over the crucible, and hold the paper over this, and start burning by bringing a Bunsen flame to it as it is held. The paper will burn first with flame, and then smoulder until all the black carbon is consumed, and a greyish ash remains of the same shape, but much smaller than the original roll of paper. (See Fig. 40.) *All* the carbon of the paper *must* be consumed. At this stage it should be dropped into the crucible itself. (For ordinary accurate work, the amount of ash given by any sample of filtering paper must be ascertained.*)

* *Ash in Filter Papers.*—The mineral matters in ash of filter papers is an almost constant quantity, and is generally ascertained once for all when commencing to use filter paper for quantitative purposes.

The best plan is to take several—half a dozen—filter papers, place them in a weighed crucible, either porcelain or platinum, put on the lid, and heat up until combustible gases escape. When the gases cease to escape and burn, but not before, take off the lid, and allow to smoulder away with the flame under, until every visible particle of charcoal has disappeared. Close, cool,

The crucible, now containing the precipitate and what adhered to the paper, and the paper ash, is placed on the pipe-clay triangle and heated with the Bunsen flame to redness. In this particular case it is necessary to make sure that the substance dealt with is *all* silver chloride. The filter paper holds a little, and during the burning this *may* become silver. It can be converted into the chloride in several ways—by blowing a little chlorine gas into the crucible, or by putting *one* drop of nitric acid on the ash, allowing to stand for
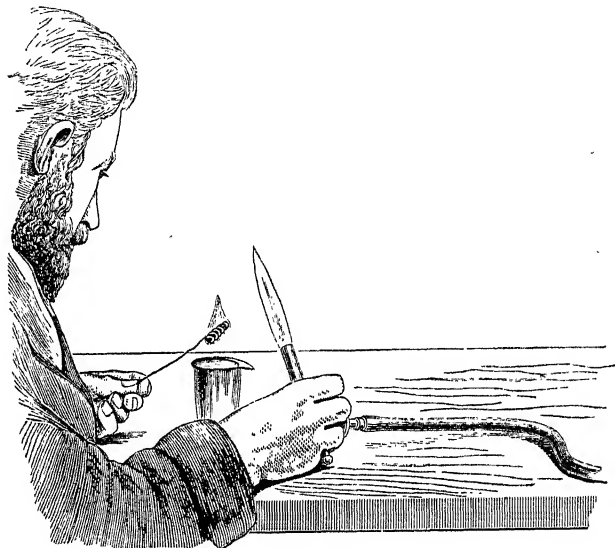
FIG. 40.

five minutes, and then adding a *very* small quantity of ammonium chloride before heating over the flame.

The crucible and chloride is now weighed, and the amount of chlorine in the salt taken calculated from the formula $AgCl = 108 + 35·5$.

and weigh. Divide the weight found by the number of filters taken, which gives the weight (nearly) of one filter. This weight is deducted from that of any precipitate which has been burnt with a filter paper.

Example.

Platinum crucible and five filter papers.

Crucible	.	.	.	.	.	.	20·1635
Crucible and ash	.	.	.	.	.	.	20·1672
							·0037/5

gives ·0007 as the ash in a No. ⊙ Swedish paper. This is a small paper. The ash of the usual size to fill a 3-inch diameter funnel weighs about ·0046.

Filter papers *must always be smaller*, when folded, than the glass funnel, so that in washing the liquid can, if necessary, cover the top edge of the paper, and thus completely wash out any soluble salts.

The filtrate from the silver chloride contains sodium nitrate and the excess of silver nitrate added. It should be all evaporated down in a porcelain or nickel or iron dish. If when nearly dry some iron filings be added and the whole then dried and heated to redness, the nitrate will be decomposed and sodium oxide, or hydroxide, left. On treating with water this will dissolve and give a very alkaline solution. (See " Alkali, Volumetric.")

(It is possible, with careful work, to obtain the whole of the sodium originally present in the common salt and measure its amount by " standard " sulphuric acid solution.)

The sodium sulphate, as obtained by the action of sulphuric acid on salt, may now be examined. Place the crucible in a moderate-sized beaker (say 500 c.c. capacity), add about 50 c.c. hot water, boil, and filter into a similar clean beaker. Repeat the boiling with water at least three times, passing all the liquid through the same filter. The volume will now be 200–250 c.c. Heat to boiling, and add very slowly a solution of barium nitrate (or chloride) and maintain in ebullition for fifteen or twenty minutes. The addition of 1 c.c. dilute nitric (or hydrochloric) acid is desirable. A white precipitate of barium sulphate will form. This substance is quite insoluble in dilute acids and ordinary pure water. It is a very fine powder, and requires some care in filtering. It must be washed very thoroughly, with boiling water, out of the beaker on to the filter paper.

To assist in detaching precipitates from the sides of beakers, &c., a glass rod, over the end of which a short piece of rubber tubing is tightly fixed, is very useful.

Combined rubbing and the impact of the jet of water from the wash-flask will detach most solids from the glass surfaces.

If the washing be commenced with hot water it must be continued with the same. Cold water after hot will often carry some precipitate through owing to shrinkage of the paper fibre and enlargement of the pores.

The paper containing the barium sulphate may now be placed, carefully of course, in a weighed platinum or porcelain crucible, and at once heated, either over a *good* Bunsen flame or in a muffle. The material of the paper will give off some inflammable gases and the adhering water will evaporate, but there will be no spirting if the heat be strong enough, as the water will assume the spheroidal state and quietly evaporate. The crucible may be closed with lid or not. After heating to full redness for twenty minutes the material in the crucible should be white. If black from the presence of charcoal it must again be heated in air until white. As all sulphates suffer a decomposition when heated in contact with carbonaceous substances a further precaution is necessary. To the contents of the crucible, after cooling, three or four drops of strong sulphuric acid are added, and the crucible, closed with its lid, again heated to redness, cooled, and weighed.

Assuming that the residue from heating salt with sulphuric acid was sodium sulphate, the reaction with the barium salt is shown by

$$Na_2SO_4 + BaN_2O_6 = BaSO_4 + 2(NaNO_3).$$

<div align="center">
Barium sulphate   Sodium nitrate
(insoluble)   (soluble)
</div>
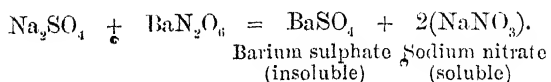
When sulphates, as this one of barium, are heated with carbon the reaction $BaSO_4 + 4C = 4CO + BaS$ is possible at certain temperatures.

This kind of action is known as "reduction."

The sulphides produced are in some cases soluble in water. They are all decomposed by sulphuric acid, a sulphate and sulphide of hydrogen being produced. Thus, $BaS + H_2SO_4 = BaSO_4 + H_2S$.

The reason for the addition of sulphuric acid to the barium sulphate in the experiment just mentioned will now be evident.

Although neither sodium nor chlorine have in these experiments been directly obtained from the salt, the compounds silver chloride and sodium sulphate indicate their presence.

The most direct method of decomposition of salt is by electrolysis of the melted substance. This can be done on a small scale sufficiently well to see but not to collect the products.

Salt is melted in an ordinary small porcelain crucible or dish (this requires a very good Bunsen burner or a gentle blowpipe flame). It is not advisable to use a platinum crucible. Attach pieces of very thin (round or square section) gas carbons by means of copper wire leads to the terminals of three or four cells (any kind, so that 4 to 8 volts are available).

FIG. 41.

If gas carbon cannot be obtained thin pieces of charcoal that has been soaked in salt solution and then dried will do.

The carbons are fitted in the tubes, as in Fig. 41. These tubes are the necks of broken distillation flasks. The side tubes serve the purpose of allowing the gas produced—in this case chlorine—to be smelt and tested with moistened litmus paper, which will be rapidly bleached. At the other terminal tiny globules of melted sodium will appear, and probably burn as soon as they come in contact with the air.

After running for a few minutes it may be possible to obtain an alkaline reaction, showing sodium hydroxide, if the negative terminal be removed, cooled, and placed in a *little* water.

A strong solution of salt may be similarly electrolysed. In this case the action is not so simple, as water takes part in the action. The first stage is probably similar to that in the melted salt, and then the "ions" or liberated particles start exchanges with the water. If the same rods and tubes be used, chlorine gas will be
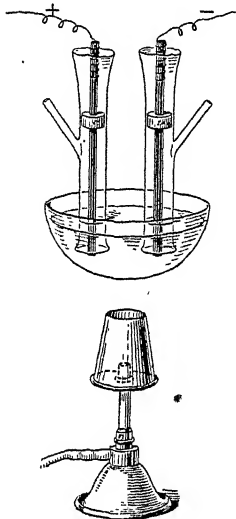
found to escape again from the + end and hydrogen from the $-$. This hydrogen is produced by the reaction $Na_2 + 2H_2O = 2NaOH + H_2$.

Other products can also be obtained (see later) if the chlorine instead of being allowed to escape be mixed with the solution by some stirring arrangement. If the "electrolysis" be conducted in a hot solution a chlorate is formed.

PRECIPITATIONS FROM SOLUTION.—When one substance is precipitated from a solution by another several additional operations are necessary before it can be weighed. One of the simplest examples is the precipitation of a metal, as oxide or hydroxide or carbonate, and final conversion of this by heating into pure or anhydrous oxide of definite composition. Oxides are generally (see *ante*) capable of withstanding a high temperature without change, and the advantages of this are that they may be obtained absolutely free from moisture, and that any volatile matters which may by accident be present are driven off during heating.

Many of the heavier metals can be precipitated as hydroxides from solutions of their salts by means of the alkali hydroxides KHO or NaHO. There are exceptional cases where these hydroxides cannot be used owing to the formation of soluble compounds. Thus sodium hydroxide cannot be used with zinc or aluminium or lead. Ammonia, also, or ammonium hydroxide, cannot be employed in some other cases, such as with copper, cobalt, nickel, zinc, for the same reasons. It is even necessary in the cases mentioned to remove all ammonium salts, and precipitate with sodium or potassium hydroxide or carbonate. The carbonates are more generally applicable than the hydroxides, zinc and aluminium oxides dissolving, for instance, in sodium or potassium hydroxides.

Copper Precipitated as Hydroxide from the Sulphate.
Example (actual).
(Part of complete analysis; see water in same, *ante*, p 60.)

Weighing bottle + copper sulphate = 30·0318
  „   „   -   „   „   = 28·6708
     Amount of salt taken = 1·3610

Dissolved in hot water in beaker (150 c.c.), heated nearly to boiling, and added, in very slight excess and gradually, potassium hydroxide solution. (The KHO is added in c.cs. at a time, and the precipitate allowed to settle between each addition. It must be kept nearly at 100° during the precipitation and filtration.) Boiled for ten minutes, allowed black precipitate to subside, and filtered quickly through folded filter paper. Washed until wash-water no longer gave an alkaline reaction to red litmus paper.* Dried precipitate, in funnel, in oven.

* *Too* much washing can scarcely be given in any case. Small quantities of hot water several times repeated is more effective than one large dose. There is no object, however, in continuing the washing after the *precipitant* has been *completely removed*.

Detached from paper; burnt paper and heated crucible, with precipitate, and ash in the muffle for thirty minutes.

(Or the precipitate may be placed, damp, in the crucible, and this at once heated over a good Bunsen flame with free access of air until of *constant weight*.)

$$\text{Porcelain crucible} + \text{CuO and ash} = 15 \cdot 9157 \left.\begin{array}{r} \\ = 15 \cdot 4803 \\ \text{ash} = \cdot 0045 \end{array}\right\} \begin{array}{l} \cdot 4309 \\ \text{CuO} \end{array}$$

$$\frac{\cdot 4309 \times 100}{1 \cdot 3610} = 31 \cdot 66 \text{ per cent. CuO,}$$

$$\text{or} = 25 \cdot 23 \text{ per cent. Cu.}$$

The calculated amount in $CuSO_4\ 5H_2O = 25 \cdot 33$.

The sulphuric acid portion of the copper sulphate should now be precipitated in the manner mentioned under the experiments with common salt. Not more than 3 grms. of the crystals of copper sulphate are dissolved in about 200 c.c. of hot water, to which 2 or 3 c.c. of dilute hydrochloric acid have been added. The contents of beaker are then heated to actual boiling, and barium chloride solution added *slowly* until all precipitation ceases. It is then allowed to stand until the white sulphate subsides, filtered, and thoroughly washed with hot water, ignited, and treated as in the previous example (*ante*, p. 67).

Example (actual).

(Part of complete analysis of copper sulphate.)

Bottle and copper sulphate .	23·5020	Barium sulphate and ash and crucible $\big\}$	= 21·4934
,, ,, ,, .	21·4930	Crucible . . .	= 19·6107
Copper sulphate . .	= 2·0090	Ash	= ·0030
			1·8797

$$= 32 \cdot 05 \text{ per cent. } SO_3.$$

Values for three items of the copper salt—viz., water, copper (or copper oxide), and SO_4 or SO_3—will now have been obtained. From them a formula may be constructed as in cases previously mentioned —viz., dividing each percentage by the molecular or atomic weights.

Complete Results for Crystals of Copper Sulphate.

Water at 100°	.	.	.	28·90 $\big\}$ 36·12
,, 240°	.	.	.	7·32
Copper oxide .	.	.	.	31·66
SO_3	.	.	.	32·05
				99·93

ᵃ Lead may be precipitated with a mixture of ammonium carbonate and hydroxide and the precipitate obtained, a mixture of the hydroxide and carbonate of lead, after washing, drying, and separation

from the paper, heated to low redness, when it becomes lead oxide, PbO.

For this exercise it is perhaps better to commence with pure metallic lead instead of a lead salt; and the same remark applies, of course, to some other metals besides lead.

A convenient lead salt is the nitrate. It is easily formed by the action of hot *dilute* nitric acid on the metal, and is purified by several crystallisations from hot water.

The nitrate gives also the oxide when strongly heated in a porcelain crucible.

Example (actual).

        Assay lead and watch glass = 32·560
                Glass alone   .   = 31·320 ; lead taken, 1·240.

Dissolved in hot dilute nitric acid, precipitated with ammonium carbonate, with a little ammonia, as above detailed.

        Porcelain crucible .   . 21·630
        Crucible and precipitate   22·968 = 1·338 lead oxide, PbO.

Lead is one of the few metals giving a sulphate of sufficiently insoluble character to be employed as a method of precipitation or separation.

Weigh from ·3 to not much more than ·6 grm. lead nitrate, or a corresponding amount of metal, dissolve in as small a quantity of hot water as possible (20 to 25 c.c.). Keep warm, and add *normal* H_2SO_4 in slight excess. ($PbSO_4$ dissolves in very strong and in very dilute H_2SO_4, but is almost insoluble in acid of *normal* strength.) Then add about the same volume of alcohol (methylated spirit). Allow to stand for some hours in a warm place, covered of course, and then pour the *clear liquid* through the filter, afterwards washing the $PbSO_4$ on to the paper with alcohol from a small wash-bottle and fine jet. The precipitate must be washed with alcohol until no acid reaction is given by the filtrate. Place the funnel and precipitate in drying oven. Weigh a porcelain crucible. Detach the dry sulphate from the paper into crucible, roll up and burn the paper thoroughly in the wire, drop the ash into the crucible, and ignite gently either over the flame or for a short time in the muffle. Cool and weigh, and then moisten with one drop of H_2SO_4 (strong), and replace in muffle. Cool and weigh again.

It will be necessary to add a few drops of acid, nitric or acetic, when dissolving many of the salts of heavy metals in water, or a clear solution will not be obtained, owing to *hydrolysis*.

This action is particularly striking with bismuth (see later).

Sulphates of the metals zinc, iron, nickel, manganese should be made by dissolving the respective metals, or oxides or carbonates, in the acid, and the compounds purified by several crystallisations from hot concentrated solutions.

Most of these sulphates form *double salts* with the alkali sulphates, which crystallise better than the simple salts. Iron sulphate,

for instance, forms with ammonium sulphate a very characteristic double salt known as ferrous ammonium sulphate. Iron, in its higher stage of excitation, aluminium, and chromium form with the alkali sulphates a very striking set of salts known as alums. These compounds crystallise practically in the same form, and have a similar composition. Common alum is represented by the formula $Al_2 3SO_4, K_2 SO_4, 24H_2 O$; and the aluminium and alkali metal are replaceable by iron and chromium and the alkali metals (including ammonia) respectively, the resulting alums having the same general type of crystal, with but a small, regular variation in certain faces, depending on the replacing metal. They are said to be *isomorphous*.

All these sulphates, whether single or double, contain water of crystallisation, which may be expelled by heating, leaving the anhydrous salt. Some precautions are necessary in each case, as when very strongly heated the sulphates are also decomposed, leaving oxides. The addition of concentrated sulphuric acid to the strong solution of a sulphate, or to the crystals containing water, will also leave an anhydrous salt.

Zinc can be precipitated from solutions not containing ammonium salts by sodium carbonate as a basic zinc carbonate—that is, a carbonate containing some zinc hydroxide.

In the presence of ammonium salts, and for separation from some metals, zinc is precipitated from hot solutions by sulphuretted hydrogen or an alkali sulphide, the sulphide, after filtering and washing, being dissolved in an acid, as HNO_3, and then precipitated by sodium carbonate. Take not more than 1 grm. of the sulphate, dissolve in 250 c.c. water, heat to boiling, and add sodium carbonate solution in slight excess. Keep hot until the precipitate settles, filter, and wash with hot water until the washings are neutral to litmus.

A final washing with spirit facilitates drying, but the precipitate on the paper may be placed in a porcelain crucible and directly heated, taking care that air has free access.

There is some danger of zinc oxide being reduced by the material of the filter paper, and as the metal is volatile at quite moderate temperatures loss may occur.

The residue after heating is zinc oxide, ZnO, which is quite infusible and non-volatile.

Ordinary metallic zinc is too impure to take directly as an exercise, and this applies to other metals, as iron or aluminium.

Zinc sulphate requires to be very strongly heated in a blowpipe flame for complete conversion into oxide.

Nickel, cobalt, and manganese may also be precipitated by sodium carbonate under similar conditions and in like manner to zinc salts.

Nickel and manganese may also be much better precipitated as hydrated peroxides; for this purpose any salt may be employed, but ammonium salts must be absent.

As an example, weigh out not more than ·5 grm. of nickel or manganese salt, dissolve in 200 c.c. water in a beaker with cover-glass,

add 20 c.c. bromine water and then sodium hydroxide until strongly alkaline, and warm *gently* for some time. A dark coloured granular precipitate will form and subside quickly. After filtering off the filtrate must be tested by again adding a little bromine water and alkali and allowing to stand.

These precipitates must be well washed with boiling water, as the alkali is pertinaciously retained.

They may be ignited directly in platinum or porcelain crucibles. The nickel becomes NiO and the manganese Mn_2O_3.

Iron, aluminium, and chromium can be completely thrown down in the form of hydroxides by the addition of ammonium hydroxide to their hot solutions. The alkali hydroxides KHO and NaHO cannot be used for aluminium and chromium, nor should alkali salts be present, as soluble compounds are formed.

Iron exists in two states—as ferrous hydroxide, $Fe(OH)_2$. and ferric, $Fe_2(OH)_6$. The former is soluble in ammonia and alkali hydroxides, and for this reason all ferrous salts must be converted into the ferric state, which can then give an insoluble hydroxide with either the ammonia or fixed alkali hydroxides.

The conversion of a ferrous into a ferric salt can be brought about by several methods of *oxidation* (see p. 77).

Ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_46H_2O$, is an excellent example for exercise. It contains, when pure, exactly one-seventh of its weight of iron; $392/56 = 7$.

The salt is made by mixing ordinary ferrous sulphate with an equivalent of ammonium sulphate, and dissolving in boiling water containing a very little free sulphuric acid. The concentrated solution should be rapidly cooled by placing the vessel in cold water, and shaking or stirring vigorously as before described. The crystals then formed are very small, and may be drained very completely from the liquid by a pump filter.

The first crop obtained must be recrystallised from hot water, and similarly treated whilst cooling. The crystals are finally dried by placing between several layers of blotting-paper.

Take about 1 grm. of the salt for analysis. Place in beaker direct from the weighing bottle; add 20–25 c.c. dilute sulphuric acid; warm gently, and then drop in carefully 5 c.c. strong nitric acid. A rather violent action may take place, with evolution of nitrogen oxides. Heat to boiling-point for a few minutes until all gases have escaped, and add, carefully, ammonium hydroxide in considerable excess. Allow to boil for five minutes, and then filter. Wash the precipitate well into the apex of the filter with hot water, until the wash-water gives no further reaction for ammonia, or ceases to leave a residue when a drop is evaporated on a glass plate.

Dry the precipitate in the oven; it will contract and detach itself from the paper if washed properly. Place in crucible, either porcelain or platinum, fold up and burn the paper, dropping the ash on to precipitate and crucible, and ignite strongly with the blow-pipe. If made really very hot for some time (twenty minutes) it will become Fe_3O_4. This precipitate may also be placed damp into a

crucible, preferably of porcelain, and ignited directly in a muffle or over a flame.

If only just heated to redness it will be Fe_2O_3 (150), which requires a really very high temperature for conversion into Fe_3O_4 (232).

This method of treatment does not separate iron from aluminium or chromium, but to a great extent from nickel or cobalt and zinc, if they are not present in very large amount. From manganese it is only a poor method of separation, unless repeated many times.

Ferrous ammonium sulphate when heated undergoes thorough decomposition, losing water, ammonia, and sulphuric acid, leaving ferric oxide or Fe_3O_4, according to temperature employed.

Weigh out not more than 1 grm. of the ferrous salt into a crucible. Heat for some time, until the contents appear all black when hot. Finally ignite strongly over the blowpipe flame to make sure the remanent oxide is Fe_3O_4. The result should not materially differ from that obtained by precipitation from solution.

Ferrous ammonium sulphate is an excellent alternative substance to copper sulphate for practice. The water of crystallisation, ammonia, sulphur, and iron may all be determined quantitatively.

Aluminium salts in solution are all decomposed by ammonium hydroxide, the hydroxide $Al_2(OH)_6$ being precipitated as an almost colourless, jelly-like substance, quite insoluble in warm ammonium hydroxide. (Small quantities only of the aluminium salt—1 to 2 grms.—should be taken.) It must be very well washed and be filtered hot. When cold it is more gelatinous and filters with difficulty. On igniting it becomes Al_2O_3, a whitish, infusible powder.

Chromium salts, as chrom-alum, may be treated in a precisely similar manner. The gelatinous precipitate is $Cr_2(OH)_6$, which on ignition becomes Cr_2O_3, a green powder.

Both the aluminium and chromium hydroxides may be placed, after washing, with the filter paper wet into a crucible and heated. There is no change produced in these cases by heating along with carbon.

Magnesium.—Most magnesium salts resemble zinc salts to a great extent. About the least soluble salt is the double phosphate of magnesium and ammonium, NH_4MgPO_4, which is almost insoluble in water and practically quite insoluble in dilute ammonium hydroxide, but very soluble in acids.

Magnesium sulphate, $MgSO_4,7H_2O$, or magnesite, $MgCO_3$, or even metallic magnesium, are suitable for exercise. ·2 to ·3 grm. of metallic magnesium will be sufficient, and not more than 1 grm. of the salts. Dissolve the metal in dilute HCl in a small 300 c.c. beaker, covered, add sodium hydrogen phosphate in slight excess—no precipitate should form if sufficient HCl be present. Warm gently but do not boil, and add ammonium hydroxide until the solution smells strongly. Arrange that there is not much more than 200 c.c. of liquid. Keep in a warm place for a few hours; avoid stirring after adding the ammonia. The precipitate will settle down more or less crystalline. Filter whilst warm (40° to 60 °C.), and contrive to wash the precipitate from the beaker with some of the clear filtrate from the first portion poured

in. Finally wash with small quantities of dilute ammonium hydroxide so that not much more than 100 c.c. in all are used. Allow to drain, and pour alcohol twice or more over the precipitate. Place funnel and precipitate in the steam oven and allow to dry thoroughly.

Weigh a porcelain crucible and lid. When the phosphate is quite dry it will detach almost completely from the paper by very slightly rubbing or pressing the sides of the filter paper cone together. Do this over a piece of clean, smooth, blue writing-paper. Drop as much as possible of the substance into the crucible, and carefully brush any adhering particles from the filter paper and any that have fallen on to the blue paper also into the crucible, using a small camel's-hair brush.

The filter paper is then folded up, coiled in platinum wire, and burnt separately (see Fig. 40), and the ash dropped into the crucible. The crucible, covered, may now be ignited in the muffle, or, gently, over the Bunsen flame, The salt becomes $Mg_2P_2O_7$ (molecular weight 222), from which the Mg can be calculated.

This is really a very difficult experiment, and great attention should be paid to details. Should the precipitate stick on the sides of the beaker during formation it may be necessary to redissolve in HCl and again precipitate. The pouring rod should *not* be in the beaker at the time, nor should it be stirred, and the beaker *must* be perfectly clean when commencing. The phosphate is very light and inclined to dust when dry, so care must be taken in getting it into the crucible. A platinum crucible may *not* be used.

The method of ascertaining the amount of phosphorus as phosphoric acid in a substance is practically the converse process, the phosphoric solution being precipitated by addition of an alkaline magnesium solution—ammonium magnesium sulphate or chloride with a little excess of ammonium hydroxide. In both cases all metals but those of the alkalies must be absent.

Phosphorus in iron or steel is generally first precipitated, as phosphoric acid in combination with molybdic acid and ammonia, from the nitric acid solution, and, after washing, dissolved in ammonium hydroxide, which produces ammonium phosphate and molybdate. On now adding a magnesium solution a double phosphate of ammonium and magnesium is precipitated, whilst the molybdate of ammonium is very soluble and is washed away. The after-treatment is the same in each case. (Carbon "reduces" these salts to some extent at a high temperature, so that phosphorus is vapourised and lost, or if the ignition took place in a platinum crucible it would be corroded or possibly melted in places.)

Calcium (and strontium) salts are mostly soluble. The oxalate is sufficiently insoluble in water, ammoniacal solutions, acetic acid, &c., for quantitative precipitation.

A calcium mineral, as Iceland spar, is convenient for experiment. Between ·5 and 1 grm. is weighed into a 500 c.c. beaker and dissolved in dilute hydrochloric or nitric acid, added only in slight excess. In case the solution is perfectly clear, ammonium hydroxide is added and the liquid warmed. If the liquid still remains clear,

ammonium oxalate or carbonate solution is now added, and the whole heated to about 80°C. The calcium salt settles down somewhat rapidly. It may be filtered, washed with water, dried at 100° on a weighed paper (see "Ammonia,"), but it is much better to place filter and precipitate in a platinum crucible and ignite strongly. The residue is then calcium oxide, CaO.

Strontium can be precipitated as sulphate in a similar manner to barium.

Potassium, ammonia, and a large number of bases of the ammonia type, such as aniline, $C_6H_5NH_2$, form compounds with acids, nearly all of which are soluble in water, most of them extremely so. They are characterised by reacting with chloroplatinic acid, $PtCl_42HCl$, to form a series or group of compounds of a comparatively insoluble nature. All these chloroplatinates show a close resemblance in composition. The potassium salt is represented by $PtCl_42KCl$; the ammonium salt $= PtCl_42NH_4Cl$, and with bases of the ammonia type, as aniline, $PtCl_42(C_6H_5NH_2HCl)$. These compounds are nearly all yellow in colour, crystalline, and mostly without water of crystallisation. These double salts are decomposed at a high temperature. The alkali salts leave alkali chloride + platinum, and the ammonia or amine salts platinum only, or in some cases platinum and carbon.

Sodium.—Properly speaking, there is no insoluble sodium compound that can be used for gravimetric determination. Most of its salts may be converted into the sulphate, and this weighed after heating to redness. (See " Common Salt," *ante*, 64.)

Experiment.

Ammonium chloride is purified by recrystallisation from water as described in other cases, and dried by heating in a dish until it commences to volatilise. Some of the dry salt is then placed in the weighing bottle, and about ·2 or ·5 grm. weighed into a small porcelain dish, dissolved in 20 c.c. water, 1 or 2 c.c. strong HCl and then an excess of platinum chloride solution added. (The strength of the platinum solution should be known approximately.)

The whole is then evaporated to complete dryness on a *steam or water* bath. The solid residue will be the double salt and the excess of platinum salt.

(The same treatment is to be followed in the case of a potassium salt or an amine salt such as aniline hydrochloride.)

The residue in the dish is now *moistened* with a very little hydrochloric acid and then covered with a mixture of alcohol and ether. (equal volumes of each), stirred with a glass rod and then allowed to stand a few minutes, the dish being covered with a glass plate.

In the meanwhile, whilst the salt solution has been evaporating, a small filter paper has been dried carefully in the steam oven and weighed. For this a paper must be selected and placed in the steam oven for thirty minutes; it is then put inside a test-tube " carrier " made out of two test-tubes, one of which slides moderately easily into the other (plenty of these " fitting " tubes are to be found in every box

of test-tubes). The rim around the open end of the smaller tube is removed by filing it around and warming in a very small flame. The open end of the smaller tube is then pushed into the larger. This makes a sufficiently air-tight carrier for paper and other hygroscopic substances whilst weighing (Fig. 42). The paper must be dried and weighed and dried again and weighed until the last two weighings are the same. The paper must be moistened with alcohol before commencing to filter the platinum salt. A mixture of alcohol and ether must be used to wash all the insoluble platinum salt on to the paper from the dish and also on the paper, until it comes through colourless and leaves no residue on evaporation. (The filtrate containing the excess of platinum chloride is saved.)

The funnel and paper are placed in the oven to dry and then in the carrying tubes to weigh. The drying and weighing must be repeated until the weight is constant.

The difference between the weight of the carrier + paper and carrier + paper + salt gives the weight of the latter.

A check on the work is obtained by now igniting the precipitate and paper in a weighed platinum (or porcelain) crucible. If the salt

FIG. 42.—Fitting test-tubes for carrying filter papers, &c. &c., for weighing.

taken was of ammonia or an amine base, platinum black only will be left. With a potassium salt potassium chloride also remains.

Generally the platinum is so coherent that the potassium salt may be washed away with warm water and the platinum left. After again heating the crucible can be weighed and the equivalent of base or metal calculated from the weight of platinum.

$$194\cdot34 \, Pt = 2 \times 39 \, K, \text{ or } 2 \times 18 \, NH_4.$$

Many salts of potassium and ammonium in addition to the chlorides mentioned will give the chloroplatinate precipitate when a sufficient excess of the chloroplatinic and hydrochloric acids are present.

OXIDATION.—Sulphur and most metallic sulphides can be *oxidised* in such manner that the sulphur is converted into sulphuric acid or into a metallic sulphate, as the case may be.

In the majority of cases sulphates, if formed, are soluble. Barium and lead are very insoluble; and a few substances, as tin and antimony, &c., may be troublesome, as they form somewhat insoluble oxides.

A number of compounds are able to function as *oxidising* agents either in aqueous solution or when melted—nitric acid, aqua regia, alkali permanganate or chlorate, bromine or chlorine and water, melted alkali hydroxides, as KHO, nitre, KNO_3, peroxides of the alkalies, as Na_2O_2, &c.

Sulphur or metallic sulphides must be very finely powdered, or the action with aqueous oxidants may be exceedingly slow.

Weigh into a beaker about ·2 or ·3 grm. of sulphur. Add to this about 10 c.c. strong nitric acid, cover beaker, and heat until an action, shown by evolution of red fumes, begins. *One or two* small crystals of potassium chlorate may be added from time to time until all signs of suspended sulphur have disappeared.

The liquid is then diluted to at least twice its bulk, boiled, to expel any oxides of chlorine or nitrogen, for a few minutes, and while still boiling barium chloride solution added in such small quantities that the liquid continues in ebullition. Barium sulphate will then precipitate in a granular form, which is easy to filter off. It must be washed and ignited and treated as before described. According to the atomic weight of sulphur and the molecular weight of barium sulphate, 32 parts of sulphur should give 233 of barium sulphate; therefore ·3 grm. of sulphur will produce more than 2 grms. of the sulphate.

Gunpowders of various kinds are perhaps better for this exercise than pure sulphur. Black gunpowder contains nearly 10 per cent., and the brown varieties from about 2 per cent. to 5 per cent. Of these 1 to 2 grms. should be weighed and treated in the manner described above, but employing more nitric acid. Gunpowders contain carbon compounds which produce coloured solutions as the oxidation is proceeding. When *all* the carbon and sulphur is fully oxidised the liquid becomes *colourless* and *clear*. This stage *must* be attained *before* addition of barium chloride. This treatment can be applied to all " organic " compounds containing sulphur.

A metallic sulphide, such as the copper sulphide, made by heating the metal in sulphur vapour (see *ante*, 56) can also be dissolved and oxidised by a mixture of nitric and hydrochloric acids (aqua regia).

About 1 grm. of the finely powdered sulphide is placed in a flask of 250–300 c.c. capacity, a small funnel being placed in the neck. 10 c.c. of nitric acid (1·3 sp. gr.) is first added, warmed gently, and when the reaction appears to slacken 10 c.c. of strong hydrochloric added. Afterwards the acids may be added alternately, 1 c.c. at a time, until all is dissolved and the solution becomes clear. Addition of very small quantities of potassium chlorate generally helps the oxidation and solution.

Before addition of the barium salt the liquid must be diluted with at least an equal volume of water, as barium salts are not very soluble in strongly acid solutions.

Melted potassium nitrate may also be employed for the oxidation, of sulphides of metals. In this case it is advisable to dilute the oxidising agent with sodium carbonate, to moderate the action. Or a mixture of alkali hydroxide and nitrate or peroxide may be used in some cases.

A convenient mixture consists of 4 parts dry sodium carbonate and 1 part potassium nitrate. 5 to 6 grms. of this mixture are placed in a porcelain crucible, and the finely powdered sulphide (say 1 grm.) added and mixed slightly by means of a wire carefully stirred in.

It is then gently heated until in quiet fusion, when cold placed in a beaker, covered with warm water acidified with dilute nitric acid (care being taken to prevent loss by covering the beaker), heated to boiling, and the sulphate of barium formed, as before, by addition of barium nitrate or chloride.

Where fusion with alkali salts is resorted to the final washing of the barium sulphate must be continued until no residue is left on evaporating a few drops of the filtrate.

The analysis of metallic sulphides to obtain quantitatively the content of sulphur and metal involves special treatment where (as with lead and others) insoluble sulphates or oxides are formed.

OXIDATION OF METALS.—Tin and a few other substances, as antimony, arsenic (tungsten), are oxidised by nitric acid.

Tin yields a hydroxide of complicated constitution, generally expressed by the formula $Sn_5O_5(OH)_{10}$, which is quite insoluble in water and nitric acid. On ignition it becomes SnO_2.

Antimony and arsenic produce oxides which on hydration form acids.

The tin in the *alloys*, or compounds of tin with metals, is also converted, on treatment of the alloy with nitric acid, into this insoluble compound, whilst nearly, if not all, the metallic nitrates are very soluble compounds. Consequently the amount of tin contained in an alloy of that substance can be ascertained by dissolving a weighed amount in nitric acid and filtering off the insoluble tin compound, which is afterwards converted by heating into tin dioxide, SnO_2.

Commercial tin is generally pure enough for experiment. The ordinary bronze coinage contains a definite quantity of tin (about 4 per cent.). Some bronzes contain 9 to 10 per cent.

The metal taken should be either in the form of turnings or filings. 1 to 3 grms. should be weighed into a beaker of about 500 c.c. capacity, provided with a concave cover-glass. Place 20 or 30 c.c. of water on the metal, and then add 20 c.c. of nitric acid (of about 1·4 sp. gr.). A violent action will generally set in and the liquid become clouded from the suspended tin hydroxide.

The temperature will rise during the solution of the metal, and must be kept up until all action is over. Finally the liquid is diluted with twice its bulk of water, and then boiled for at least ten minutes before filtering.

The precipitate is very fine, and needs a good filter paper. It must be washed with *hot* water or very dilute hot nitric acid until a drop of wash liquid leaves no residue when evaporated on a glass plate.

The precipitate may be dried and detached from paper before igniting, or placed direct in a *porcelain* crucible and heated, without the lid, over a flame or in a muffle. The product should be quite white. Any colour indicates imperfect washing.

The formula SnO_2 implies that in 150 parts 118 are tin and 32 oxygen.

REDUCTIONS.—Chromium, manganese, and some other substances form several very distinct classes of compounds, in one of which the element acts as base and is combined with some acid, and in another it acts as an acid and is combined with some base.   Chromium can pass very easily from the one form to the other.   From chromates and bichromates, &c., the chromium cannot be precipitated as hydroxide. When any of these compounds are brought in contact with a substance capable of taking up oxygen they give up a definite amount and become *reduced* to chromium salts.   Alkali bichro- -mates are largely used in a number of technical operations as oxi- dising agents.   The commercial salts are not quite pure.   20 or more grms. of the potassium salt should be dissolved in boiling water, the liquid filtered hot, then cooled rapidly, with constant agitation, and the fine crystals drained on a pump filter.   The crys- tals do not contain water of constitution.   The moisture may be driven off by direct heating, and at a moderate temperature the salt melts to a red liquid, which sets on cooling into an orange-red crystal- line mass which easily breaks up.

Weigh *not more* than ·5 of the salt from a weighing bottle into a 500 c.c. beaker.   Dissolve in about 100 c.c. hot water, add 5 c.c. hydro- chloric acid, and then about the same amount of alcohol.   Cover the beaker and heat to boiling.   The colour of the liquid will change from orange to green, and a strong odour of aldehyde will be noticed. The solution must be boiled until the aldehyde odour has passed away and the liquid is of a pure green colour.

Add slowly a few c.c. strong ammonium hydroxide, keeping up the heating.   A grey-green precipitate should form.   Filter as hot as possible and wash very thoroughly with hot water.   It is an advantage if this operation of precipitation and filtration be done quickly, as chrom-ammonias are liable to form on long exposure to air   This will be seen by the filtrate becoming purple.   It should be perfectly colourless.   The precipitate cannot be too well washed.

The filter paper and precipitate may be introduced at once, after draining, into a platinum crucible, and heated either in a muffle or by a blowpipe flame.   The final result is Cr_2O_3, which should be dark green in colour and a perfectly loose powder.

Instead of alcohol, a sodium thiosulphate solution or yellow ammonium sulphide or sodium sulphite may be used for the reduc- tion.   Some sulphur is thrown down from the former of these, but it does not interfere, being burnt off in the ignition.   It is, however, more difficult to filter.

Many chromates or bichromates may be made by double decom- position from the potassium salt and other metallic salts, as silver nitrate, &c.   Sodium bichromate is much more soluble than the potassium salt, and is also deliquescent.   If the sodium salt is taken for experiment two or three hundred grams will be required for crystallisation, and the salt after draining and fusing must be kept in a closed bottle.

CHAPTER VII.

VOLUMETRIC ANALYSIS.

THE object of volumetric analysis is to ascertain, quantitatively, the composition of a given substance by means of solutions of a reagent of known strength. Certain characteristic and visible reactions are produced, and from the *volume* of reagent used the amount of substance present may be deduced from the laws of chemical equivalence. All that is necessary for the successful performance of the analysis is that the exact termination of the reaction shall be in some way made visible.

The apparatus required for volumetric processes is generally of a simpler character than that employed for gravimetric analysis. In addition, the estimation may be performed very rapidly, and with an accuracy quite equal to that obtained by the most careful gravimetric methods, and in some cases even more so.

End of Reaction.—As previously mentioned, the success of any volumetric analysis depends upon the termination of the reaction being definite and observable. The most general methods of ascertaining this may be classified as follows:

1. *The appearance or disappearance of a distinct colour in the liquid under operation.*—An example of this is to be found in the behaviour of iron salts towards potassium permanganate. If a permanganate solution be added drop by drop to an acid solution of a ferrous salt, the colour is discharged so long as the latter is in excess. When the permanganate strikes a distinct colour in the liquid the oxidation of the ferrous salt has been completed. Conversely, when hydrogen peroxide is added to a solution of permanganate the colour of the latter becomes fainter, and finally disappears at the moment the reaction is complete. In both cases the final change is brought about by one or two drops of solution, which may be extremely dilute.

2. *When a precipitate just ceases to form.*—An example of this is afforded by a method of finding the amount of silver in a substance. If a solution of sodium chloride be gradually added to a silver solution, the latter being constantly shaken so as to allow the precipitate to subside, a point will be reached at which a drop of the salt solution ceases to cause a further precipitation. This indicates the end of the reaction.

6

3. *By the use of an indicator*, which may be defined as a substance which renders the end reaction evident, without itself appreciably interfering with the reaction.   Examples of these are provided by the estimation of the acidity or alkalinity of a given solution; and as this is one of the most frequent uses of volumetric analysis, the names and properties of the chief acid and alkali indicators will be given:

(*a*) *Litmus.*—The solution of litmus, as is well known, is turned red with an acid and blue with an alkali.   If one be added gradually to a solution of the other, into which a little litmus has been poured, a point of neutrality will be reached when the litmus is neither red nor blue (a purple tint), after which one drop of acid or alkali will turn it red or blue.   The end of the reaction is thus made evident. The objection to litmus is that it is affected by carbonic acid, so that in such cases as the examination of carbonates with an acid the litmus is turned prematurely red.   Boiling the solution during the process obviates this.

(*b*) *Methyl orange* (para-sulpho-benzene azo-dimethylaniline) is an orange-coloured compound, soluble in water.   It becomes red on the addition of an acid.   It should be made by dissolving 1 grm. of the solid in a litre of distilled water.   One drop of this solution present in an alkaline liquid will strike a red tint immediately an acid is added in excess.   It is probably the best indicator for acids and alkalies, being totally unaffected by carbonic acid or sulphuretted hydrogen.

(*c*) *Phenolphthalein.*—This indicator is prepared by dissolving 5 grms. of the powder in 1 litre of 50 per cent. alcohol.   A few drops of this solution show no colour in a neutral or acid solution, but the faintest excess of alkali produces a deep purple-red.   It is, however, affected by CO_2 and H_2S.

The indicators used in other volumetric processes are too numerous to classify here; such as are used in the processes to be described will be found, with the principles of their action, in the description of the analyses.

STANDARD SOLUTION.—A standard solution may be defined as an arbitrary solution possessing a known chemical strength.   Such solutions are generally, though not always, made in accordance with the chemical equivalent of the reacting body, as explained in the next definition.

NORMAL SOLUTION.—A normal solution is one which possesses the hydrogen equivalent of the reacting element in grams per litre.   It is generally expressed by the symbol N.   Reference to examples will make clear the definition given.

1. Sodium hydroxide, NaOH, consists of 23 parts by weight of sodium, 16 of oxygen, and 1 of hydrogen = 40.   A litre of normal sodium hydroxide contains 40 grms. of NaOH, and therefore 1 grm. of hydrogen.

2. Sodium carbonate, Na_2CO_3, contains 46 parts by weight of

sodium, equivalent to 2 grms. of hydrogen. For a normal solution the weight expressed by Na_2CO_3 divided by 2 will give the amount in grams to be contained in 1 litre.

3. Copper sulphate, $CuSO_4$. contains 63 parts by weight of copper. The equivalence of copper to hydrogen is $32\cdot5 : 1$, as copper is divalent. The number of grams in a litre of normal copper sulphate is therefore one-half of the number represented by $CuSO_4$.

It is of great importance that this point should be clearly understood, in order that a thorough insight into the various volumetric processes may be obtained.

The chief advantages obtained by making standard solutions of normal strength are that any two such solutions, capable of reacting upon each other, do so in exactly equal volumes, and that the final calculations are rendered much easier.

It is often an advantage to employ solutions of less strength than normal. In such cases they are usually made some simple fraction of normal; thus, decinormal $(\frac{N}{10})$, seminormal $(\frac{N}{2})$, &c.

All standard solutions must be kept in well-stoppered bottles. Before using for an analysis they should be well shaken, as evaporation from the surface of the liquid causes a deposition of water on the sides of the bottle, leaving the remaining solution unduly strong.

Titration.—The actual operation of running in a standard solution to the liquid undergoing analysis and the observation of the end reaction are expressed by the term "titration." The solution is run in from a graduated instrument, the burette (see Introduction). By this means the amount of solution used is accurately known. The solution undergoing examination may be contained in either a beaker, flask, or dish. Whichever of these is used, it is essential that constant mixing shall take place, in order that every part of the liquid may participate in the reaction. This may be accomplished in the case of a flask by swishing round the contained liquid and then slightly inclining; in open vessels a glass stirring rod may be used. The instrument from which the standard solution is delivered must never be so far removed from the test liquid as to cause splashing; nor should the solution be allowed to run down the side of the beaker or flask, as difficulty is experienced owing to the adhesion of the solution to the side of the vessel.

The details of the titrations given will be found under the respective headings.

Graduated instruments.—The three chief graduated instruments required in volumetric analysis are the pipette, the measuring flask, and the burette (see Introduction).

The pipette, as shown in the sketch, consists of a narrow piece of tubing widened out at the centre. The bottom portion of the narrow tube is drawn out to a moderately fine taper point, so as to allow the liquid to be retained when the opposite end is closed, and also to ensure a moderately slow delivery of the contents. The graduation consists of a mark on the upper portion of the narrow tube.

To use the pipette, the point is immersed in the liquid from which an exact volume is to be transferred to another vessel. Suction is then applied, using the tongue as a valve, until the liquid rises two inches or more above the mark. The forefinger is then rapidly placed over the open end, when, by gently moving the finger, air may be slowly admitted and the column allowed to sink until the bottom of the meniscus is opposite the mark. The finger is then pressed tightly, and the pipette removed bodily and its contents discharged in the receiving vessel by lifting the finger. The last drop remaining in the tapered portion may be expelled by touching it against the side of the vessel, closing the top with the finger, and grasping the wide portion with the hand. The warming expels the last drop. The pipette is evidently made to *deliver* a given volume; its actual contents are obviously greater, as it is wetted by the liquid and therefore retains a portion on its sides. Before using the pipette for a different solution, it should be rinsed out with distilled water several times, dried, and rinsed out with the new solution before final filling. Care must be exercised during the last stages of filling, otherwise the solution may be drawn into the mouth. A few inches of small rubber tube at the top of the pipette is most convenient.

Convenient sizes of pipettes are 100 c.c., 50 c.c., 25 c.c., 20 c.c., 10 c.c., and 5 c.c.

Measuring flasks (see Introduction) may be obtained in various forms and sizes. In preparing standard solutions such flasks are absolutely necessary. Mostly these instruments are graduated for the ordinary temperature of 15°–16° C., and all the operations of volumetric analysis should be performed with the liquids at as near these temperatures as possible. Liquids expand appreciably with slight increase of temperature. The flasks are of such a size that the graduation mark may be placed on the neck. The best forms are provided with an accurately ground glass stopper, so that any solution contained in the flask may be mixed and preserved from evaporation. The stoppered flask, however, is not absolutely necessary. Such flasks are usually made to *contain* a given quantity; the amount they will deliver is obviously less, and should a flask be used for the latter purpose it must be specially graduated.

Convenient sizes are 1 litre, 500 c.c., 250 c.c., 200 c.c., 100 c.c., and 50 c.c.

In filling to the mark the last few drops should be blown in from a wash-bottle jet. Where it is only requisite to measure or deliver quantities of liquids roughly, measuring cylinders are used. They consist of cylinders graduated by divisions marked on the side, and should possess a lip for convenience of pouring. Such cylinders are of great service in the rougher portions of the work involved in volumetric analysis.

Convenient sizes are 250 c.c. and 100 c.c.

The Burette (see Introduction).—There are numerous forms and sizes of this instrument obtainable, but the best form for general use consists of a graduated tube with a tap at the bottom, which by

careful turning may be adjusted so as to allow only a single drop to escape.

A convenient size for ordinary use is the one graduated in tenths to 55 c.c. Two drops are about equal to $\frac{1}{10}$th of a c.c. The method of using the burette is as follows: Pour in a few cubic centimetres of the solution to be used, and incline the burette so that every portion is washed in turn by the liquid. This washing liquid is now poured away, and the burette filled to a few centimetres above the zero mark. It is then clamped in a stand, and the tap rapidly turned on full and closed again. This operation expels the air bubble in the tapered tube beneath the tap. The eye is now placed on a level with the zero mark, and the tap gently turned so as to allow a very gradual escape of the liquid. The column falls slowly, and when the bottom of the meniscus is exactly opposite the zero mark the tap is closed. The drop clinging to the bottom is removed by touching with a glass rod, when the liquid to be titrated may be placed beneath the burette. If the amount of solution required for the reaction be approximately known, this amount minus about 2 c.c. may be run in at one operation. The final stage of the reaction is found by running in two drops at a time, stirring the solution with a glass rod after every addition. A point will be reached when the addition of a given two drops will cause the indicator to turn colour, at which stage the reading of the burette is taken by observing the mark opposite the bottom of the meniscus, holding the eye level with the mark. When nothing is known as to the strength of the liquid to be titrated, an approximate idea must be obtained by running in 1 c.c. at a time, when the end reaction will be found between the limits of a c.c. The burette must be again filled with solution, and a second titration performed accurately, the last portions of the solution being run in drop by drop until the reaction is seen to be completed.

When the burette is to be used for another solution it should be rinsed out several times with distilled water and dried. It may then be rinsed out with the new solution, and filled and run down to the zero mark as before.

The drop clinging to the bottom of the burette during the titration may be transferred to the liquid by touching with the stirring rod and immersing the latter in the liquid undergoing titration. When the end of the reaction is close at hand, this drop frequently suffices to complete the change of tint in the indicator.

The burette may be filled directly from the bottle containing the solution by holding it vertically, and allowing the lip of the bottle to rest on the top. The solution must be poured in gently, otherwise it will flow over the outside of the burette. With a little care and practice, however, the burette may be filled in this manner without danger of overflowing.

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Convenient sizes are 1 litre, 500 c.c., 250 c.c., 200 c.c., 100 c.c., and 50 c.c.

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When the burette is to be used for another solution it should be rinsed out several times with distilled water and dried. It may then be rinsed out with the new solution, and filled and run down to the zero mark as before.

The drop clinging to the bottom of the burette during the titration may be transferred to the liquid by touching with the stirring rod and immersing the latter in the liquid undergoing titration. When the end of the reaction is close at hand, this drop frequently suffices to complete the change of tint in the indicator.

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For all ordinary volumetric estimations it is only necessary that the readings of the burette be taken to $\frac{1}{10}$th of a c.c., as this amount is frequently necessary to make the change in the indicator abso-

lutely certain. For more refined methods Erdmann's float may be used, by means of which readings to $\frac{1}{20}$th of a c.c. may be accurately observed. This consists of a weighted glass tube having a mark round its circumference. After roughly filling the burette the float is dropped into the liquid, when the mark will be seen to be below the surface. To adjust the burette for titration the tap is first rapidly and then gradually turned as before, until the mark on the float is opposite the zero mark. The final reading is taken after titration by observing the graduation opposite to the mark on the float.

PREPARATION OF NORMAL ACID AND ALKALI.—A normal
acid and alkali are frequently used in volumetric analysis, and their preparation should form one of the first lessons of the student. By accurately following the instructions given, correct solutions may be made by the beginner.
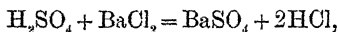
(1) Normal sulphuric acid.

$$\frac{H_2SO_4 = 98}{2} = 49 \text{ grms. per litre.}$$

Strong sulphuric acid, as purchased, having a specific gravity of 1·84 at 15° C., has a strength of about 36 times normal; 1 c.c. diluted to 36 c.c., or 27·8 c.c. diluted to 1 litre, would therefore possess a strength approximating to normal.

Place about 900 c.c. of distilled water in a litre flask, and pour in 28 c.c. of the strong acid, stirring with a glass rod, in order to mix thoroughly. Allow the mixture to become quite cool, lift the rod out of the liquid and wash with a jet of water from a wash-bottle, and add water up to the mark. The mixture should now be poured into a large, dry beaker, and stirred with a glass rod or strip to ensure thorough mixing.

A sample of the solution must now be tested in order to accurately determine its strength.

(a) Standardising the acid by precipitation as barium sulphate.—For this purpose 10 c.c., or better 20 c.c., of the acid are transferred to a beaker by means of a pipette, diluted with water, heated, and precipitated by the addition of barium chloride. The precipitate is treated as before described. For the acid to be strictly normal, the weight of the precipitate of $BaSO_4$ should be exactly 1·165 grms., if 10 c.c. were taken, and 2·33 if 20 c.c., as may be calculated from the equation,

$$H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl,$$

remembering that the weight of real acid in a litre of normal sulphuric acid is one-half of that represented by the formula H_2SO_4. Two such precipitations should be performed; if these agree the acid may be diluted or strengthened, according to the figures obtained, so as to make its strength exactly normal.

Example (actual).

10 c.c. of acid prepared as above gave with barium chloride a precipitate weighing 1·1824 grms.

Check 10 c.c. gave 1·1818 grms.

Mean = 1·1821 grms.

The acid was therefore too strong in the proportion of $\frac{1\cdot1821}{1\cdot1650} = \frac{1\cdot0147}{1}$. It was therefore necesssary to add 14·7 c.c. of water to every litre of solution to make the acid strictly normal. After dilution and mixing 10 c.c. yielded 1·1642 grms., showing that the acid was as nearly as possible normal.

(b) *Standardising the acid by means of sodium.*—A piece of sodium is freed from naphtha by pressing between the folds of filter paper. It is then cut rapidly with a knife so as to present a perfectly clean surface on all sides, and transferred by a knife to a stoppered weighing bottle (whose weight has previously been determined), and then weighed. From three-quarters of a gram to a gram will be found a convenient quantity for this experiment.

The sodium is now dropped from the weighing bottle into a flask of about 350 c.c. capacity, containing about 100 c.c. of pure alcohol in which the sodium dissolves quietly. The flask should be inclined, so that a stream of water may be allowed to run over it while the sodium is dissolving. After the sodium has dissolved the solution is diluted with its own bulk of water, and a few drops of methyl orange indicator or litmus added. The acid to be tested is now run in carefully from a burette until the indicator just turns colour. The approximate amount of acid required being easily calculated from the amount of sodium taken, one titration will be sufficient if the last two or three cubic centimetres be added gradually. The acid is then corrected to normal by adding the requisite amount of water or strong acid, as indicated by the calculation. Instead of adding more acid, the liquid may be evaporated or boiled down. Water only evaporates, so that the solution of acid becomes stronger.

Example (actual).

0·6210 grm. of sodium required 25·8 cubic centimetres of acid.

Check 0·7130 grm. required 29·7 c.c.

From the definition of a normal solution 23 grms. of sodium should require 1000 c.c. of normal acid; therefore 0·621 should require $\frac{1000 \times 0\cdot621}{23} = 27\cdot0$ c.c., and 0·713 should require $\frac{1000 \times 0\cdot713}{23} = 31\cdot0$ c.c. The acid was therefore too strong in the ratio of $\frac{27}{25\cdot8}$ or $\frac{31}{29\cdot7}$ and was diluted by adding 12 c.c. of water to every 258 c.c. of acid, as indicated by the first ratio. After mixing it was again tried, when 0·658 grm. of sodium required 28·6 c.c. of acid, showing it to be strictly normal.

The sodium method in careful hands is very good, and takes but

a short time. Unfortunately all samples of sodium are not quite pure.

Another method is to weigh out a few grams of pure dry sodium carbonate, dissolve in a known volume of water, and titrate hot, if litmus be used as indicator (see below).

Copper sulphate can be obtained, as before described, in a very pure state by recrystallisation. When a solution of this salt is electrolysed, using platinum pole plates, pure sulphuric acid is left. 249 grms. of the salt should yield 98 of sulphuric acid.

It will be evident that quite a small quantity, say 2·49 grms., will give sufficient acid to fix the strength of an alkali solution.

It is not advisable to attempt to weigh out this quantity, but to take a quantity in that region and calculate the amount of water required for dilution to standard strength.

Having obtained an exactly normal acid by the above means, a normal alkali may readily be obtained, as it is only requisite to adjust the strength so that it exactly neutralises an equal volume of normal acid. For a normal alkali either pure sodium carbonate or sodium hydroxide may be used.

Preparation of normal sodium carbonate :

<div align="center">

(2) Normal sodium carbonate.

$$\frac{Na_2CO_3 = 106}{2} = 53 \text{ grms. per litre.}$$

</div>

A quantity of pure anhydrous sodium carbonate is gently heated in a platinum vessel and allowed to cool. 53 grms. are then accurately weighed and dissolved in water in a beaker. The solution is then transferred to a litre flask, the beaker washed and the washings added, and water then added up to the mark. It is mixed by pouring into a dry beaker and stirring, and returned to the flask. To test its accuracy 50 c.c. are measured out in a pipette and transferred to a beaker. About 200 c.c. of water are added, and a few drops of methyl orange indicator. The normal sulphuric acid previously prepared is run in from a burette, when exactly 50 c.c. should be required. If too strong or too weak, the amount of water or sodium carbonate to be added may be calculated as previously explained.

The sodium carbonate may also be taken as the standard substance, and the acid strength fixed or based upon it.

NOTE.—A beaker or flask of at least 500 c.c. capacity should be used for this titration, so as to avoid loss by spirting caused by the evolution of *carbon dioxide gas*.

If the strength of the sulphuric acid has been fixed by the barium sulphate method the alkali solution may be more quickly made by dissolving *about* 43 grms. of sodium hydroxide in water and making up the volume of solution, after cooling to 15° C., to 1 litre. On testing this against the acid it will be found too strong. Perhaps 46 c.c. of the sodium hydroxide solution will neutralise 50 c.c. of the acid, in which case every 46 c.c. of the alkali solution will evidently

require the addition of 4 c.c. water to reduce to correct strength. This principle will now be readily understood.

By the aid of a standard acid and alkali a great number of experiments may be performed. A good exercise is to find the strength in *normals* of some of the common laboratory reagents. Thus the strong hydrochloric acid, of sp. gr. 1·16, will be found to be about 10 N; the strong nitric acid, of sp. gr. 1·42, 16 N; the strong ammonium hydrate, sp. gr. ·88, 17 N; and so on. Quantities should be taken so as to require about 50 c.c. of the standard acid or alkali so that the operation may be performed without having to refill the burette; such quantities may be calculated roughly by reference to the figures given. In doing this several grams or cubic centimetres of the strong acid or alkali are diluted or dissolved in water up to a considerable, but of course accurately known, volume. For instance, if 20 grms. of sulphuric were weighed, then 500 or even 1000 c.c. would not be too great a volume for it to be diluted to for titration. A knowledge of the chemical strength of reagents is thus obtained, and the amount required to dissolve any given substance may be easily deduced. For example, if it be required to know how many c.c. of strong HCl are required to dissolve 10 grms. of chalk, it is seen from the equation

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$
$$ 100 71$$

that 100 grms. of chalk require 71 grms. of HCl = 2 litres of N. HCl. Therefore 10 grms. require 200 c.c. of N. HCl = 20 c.c. of 10 N or strong acid. The value of such calculations is quite evident.

Ammonia solution, nitric acid, and other fuming liquids must be weighed in small stoppered bottles, as when exposed to air they are losing strength every minute. In the case of ammonia (ammonium hydroxide) it is, for the same reason, advisable when titrating to quickly add to an excess of acid, and this *excess* ascertained by the addition of normal alkali. As the two solutions match they are like the arms of a balance. If too much of one, acid, be used, the excess can be neutralised by the alkali, the difference being due to the substance under trial. Thus if 10 c.c. of a weak ammonia solution be put into 50 c.c. of N acid it is much more than neutralised, and may require the addition of 35 c.c. of N alkali to balance. The quantity of N acid used on the ammonia solution was therefore 50 − 35 = 15 c.c., or the 10 c.c. contained 15 × ·017 NH₃.

In performing a titration of, say, a sodium hydroxide sample weigh out a few grams into a beaker or dish, dissolve in a small volume of water, pour this into a graduated flask—say 500 c.c.—wash out the beaker in which the solution was made by repeated *small* quantities of water until absolutely all the substance has gone, and finally make up exactly to the mark on the neck from the wash-bottle, being careful to bring the temperature of the solution to as nearly 15° C. as possible before adding the final water. Now shake thoroughly, take 50 c.c. into a dish, dilute with three or four times

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as much water, add a few drops of litmus, and then commence the addition of N acid until the litmus changes just to red.

Suppose 7·5 grms. of a "soda" had been weighed and dissolved in 500 c.c. water, and 50 c.c. of this "soda" liquid required 8 c.c. of N acid. Each c.c. of N acid contains ·049 grm. of H_2SO_4. $\dfrac{H_2SO_4 = 98}{2}$ is equivalent to $\dfrac{2NaOH = 80}{2}$, or each c.c. of acid is equivalent to ·040 of sodium hydroxide. Therefore the 50 c.c. of "soda" are equivalent to ·040 × 8 = ·320 NaOH, and this amount was contained in 50 c.c. or one-tenth of the original substance. Therefore in 7·5 grms. of this "soda" 3·20 grms were NaOH; that is, $\dfrac{3\cdot 20 \times 100}{7\cdot 5} = 42\cdot 6$ per cent.

One advantage of making up a solution, to be tested, to a considerable volume is that the experiment may be several times repeated. The *results* may not be absolutely the same each time, but should differ but a few tenths of a cubic centimetre. The mean of three or four near results can then be taken.

Potassium permanganate is one of the most powerful oxidising agents known. Whether as a solid or in solution in water it can easily give up a certain quantity of its oxygen content. Its composition is represented by the formula $K_2Mn_2O_8$, and under ordinary circumstances five-eighths of this oxygen (= 80) is given up. It is generally necessary that an acid, such as sulphuric, be present at the same time, otherwise the oxides of potassium and manganese are liberated, and may possibly interfere with the progress of the reaction. For example, alcohol is oxidised by this substance to aldehyde and acetic acid, but unless some sulphuric acid be present some potassium acetate and solid manganese dioxide are produced. The latter somewhat impedes the reaction.

Alkali permanganates alone are soluble in water. They have very great tinctorial power. A litre of water may be tinted pink by a quantity of potassium permanganate too small to be indicated by any balance. The colour of the permanganate is the indicator. As oxygen is taken from it the colour fades. When the substance has become fully oxidised the colour of the least excess of permanganate remains. With mineral compounds, salts, &c., of metals its action is comparatively simple. Thus sulphurous acid becomes sulphuric, ferrous oxide ferric, &c. With some carbon compounds its oxidising action is sometimes more complex.

PREPARATION OF DECINORMAL PERMANGANATE SOLUTION. — The molecular weight of the potassium salt $K_2Mn_2O_8 = 316$. It is not sufficiently soluble to allow of this quantity in grams being dissolved in a litre of water, nor would such a strong solution be convenient or accurate in use. A tenth or decinormal solution, or even a centinormal one, is preferable.

As the *available* oxygen is represented by 5 atoms in the above formula, and as oxygen is divalent, or equivalent to 2H, it follows that

$\dfrac{K_2Mn_2O_8}{5 \times 2}$ will be the weight of salt in a litre of a normal solution

and $\dfrac{K_2Mn_2O_8}{100} = 3 \cdot 16$ grms. the weight of salt in a litre of decinormal strength.

Dry a quantity of pure potassium permanganate crystals by gently warming, and after cooling weigh out exactly * 3·16 grms. Transfer this to a beaker, dissolve in water, and pour the solutions into a litre flask. The crystals dissolve rather slowly, and it is advisable to pour the first water into the graduated flask after being in contact with the crystals for about five minutes, stirring being frequently resorted to. Fresh water is then poured over the remaining crystals, and so on until the solution is completed. The beaker is then thoroughly rinsed out, the washings being poured into the flask, and water added to the mark. Mix as usual by pouring into a beaker and stirring and returning to the flask.

STANDARDISING THE POTASSIUM PERMANGANATE SOLUTION.

—The best method of obtaining the exact strength of the solution is by employing ferrous ammonium sulphate, which may be obtained pure. This salt is also convenient for calculation, as it contains exactly one-seventh its weight of iron, as will be apparent from the formula, $FeSO_4,(NH_4)_2SO_4,6H_2O$, the atomic weight of iron being 56. (See also *ante.*) When acted upon by potassium permanganate in the presence of sulphuric acid, the following reaction takes place (neglecting crystal water) :

$$K_2Mn_2O_8 + 10Fe(NH_4)_2(SO_4)_2 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4$$
$$+ 10(NH_4)_2SO_4 + K_2SO_4 + 8H_2O.$$
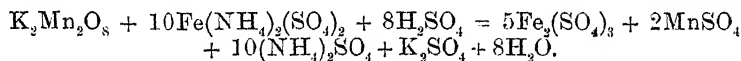
From the above equation it will be seen that 316 grms. of permanganate react with $10 \times 56 = 560$ grms. of iron. Therefore 3·16 grms., or 1 litre of decinormal solution, would react with 5·6 grms. of iron, and 100 c.c. would react with ·56 grms. of iron, and 1 c.c. react or be equivalent to ·0056 of the metal or give ·0008 of oxygen. The weight of ferrous ammonium sulphate containing this quantity of iron is ·56 × 7 = 3·92 grms. Weigh out about 1·5 grms. of the pure salt, dissolve in cold water in a beaker, and add dilute sulphuric acid to make the solution nearly normal in strength. This may be accomplished by adding to the water solution about one-eighth its bulk of 1 in 5 sulphuric acid. Then run in the permanganate solution until the addition of one drop produces a permanent pale pink colour in the liquid. The colour may be detected more easily if the beaker be allowed to stand on a sheet of white paper; better still if a white porcelain dish be employed. The amount of solution used should

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* Note that it is sometimes very difficult to weigh out any particular amount of a substance. If 100 grms. are wanted to be dissolved in 1000 c.c. water, as nearly 100 grms., say 98·7000, are weighed, and then obviously the proportionately *less* amount of water used.

be such that $\dfrac{3\cdot92 \times \text{c.c. used}}{\text{weight of salt taken}}$ should equal 100, as 3·92 grms. of the salt require 100 c.c.

Example (actual).

(*a*) 1·61 grms. of ferrous ammonium sulphate required 41·1 c.c. of permanganate solution ;

(*b*) 1·506 grms. required 38·4 c.c.

$$\frac{3\cdot92 \times 41\cdot1}{1\cdot61} = 100\cdot0.$$

$$\frac{3\cdot92 \times 38\cdot4}{1\cdot506} = 100\cdot0.$$

The solution was therefore practically decinormal.

$\frac{N}{10}$ permanganate can be employed to ascertain the amount of iron in any iron compound. The substance should be in sulphuric acid solution, and halogen salts be absent, or if present the solution be highly diluted. It is advisable that all iron solutions be well diluted. The action is particularly rapid and takes place cold.

Iron in the ferric state must be "reduced" to ferrous before the employment of permanganate. This may be accomplished in various ways.

A ferric iron solution, the sulphate, is rapidly reduced by boiling with *pure* zinc. Free sulphuric acid must be present. Aluminium or magnesium may sometimes be used for this purpose. Boiling with sodium sulphite will also reduce the iron, but care must be taken that every trace of the sulphurous acid is expelled.

OXALIC ACID, $H_2C_2O_4$, and all oxalates are oxidisable by permanganate. Oxalic acid on oxidation is decomposed into two molecules of carbon dioxide and one of water ; or $H_2C_2O_4 + O = H_2O + 2CO_2$. The molecular weight of the anhydrous acid is $2 + 24 + 64 = 90$. So that 90 grms. of the acid require 16 grms. of oxygen for oxidation. But the permanganate contains but ·0008 of available oxygen per c.c., and is therefore equivalent to ·0045 of oxalic acid. The ordinary acid contains two molecules of water.

Many metallic oxalates are insoluble in water. They as well as the free acid are oxidised by permanganate in *warm* dilute sulphuric acid solution. For experiment the acid is dissolved in water acidulated with sulphuric acid, and a measured volume heated to about 80° before the permanganate is added.

Many metals, such as calcium, the oxalates of which are insoluble in water, can be estimated by permanganate, by being precipitated as oxalate, the salt washed free from acid, mixed with dilute hot sulphuric acid and titrated hot. Calcium oxalate has the composition $CaC_2O_4 = 40 + 24 + 64 = 128$. This would require 16 of oxygen, but as the permanganate gives ·0008 per c.c., each c.c. is *equivalent* to ·0020 of calcium.

Oxalates of other metals, as copper, zinc, nickel, should be made by the student and investigated by the permanganate method.

IODINE AS AN OXIDISING AGENT.—Iodine in the presence of water acts as a gentle oxidising agent similarly to chlorine. For instance, SO_2, As_2O_3, H_2S, and many other substances can be oxidised a definite stage. On the other hand, an iodide like potassium iodide is easily oxidised, or, at any rate, decomposed so that free iodine results. The colour of free iodine is almost a good enough indication by itself, but in contact with starch an extremely small amount of iodine is made evident. With sodium thiosulphate iodine acts in a very definite manner as far as the iodine is concerned, a perfectly colourless compound being produced.

The two solutions iodine and thiosulphate can therefore be used as a sort of couple for volumetric work, and are spoken of as "iodine and thiosulphate." They can be employed both in cases of oxidation and reduction, and in consequence have a more extended application than many other volumetric solutions. The above are instances of oxidation, the action with SO_2, or sulphites, being :

$$SO_2 + 2H_2O + I_2 = 2HI + H_2SO_4.$$
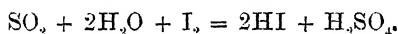
Oxidising agents, as chlorine or nitrous acid, liberate iodine from KI and other iodides. Thus : $Cl_2 + 2KI = 2KCl + I_2.$
With sodium thiosulphate the action is :

$$2Na_2SSO_3 + I_2 = 2NaI + Na_2S_4O_6.$$
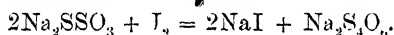
Chlorine and bromine act much more energetically than this, producing sulphuric acid as one product.

PREPARATION OF A DECINORMAL SOLUTION OF IODINE.

$$\text{Iodine} = \frac{126 \cdot 5}{10} = 12 \cdot 65 \text{ grms. per litre.}$$

Iodine as purchased is not sufficiently pure for this purpose, and must be purified before being employed. A simple method for purification is to grind up ordinary iodine with about one-fourth its weight of potassium iodide and then heat gently in a dish covered with a funnel. Pure iodine will then sublime and deposit on the sides of the funnel, any bromine or chlorine which may be present combining with the potassium and liberating an equivalent of iodine. The crystals of sublimed iodine are collected in a weighing bottle, which should be kept in a desiccator over sulphuric acid. The bottle + iodine is weighed, the weight of bottle being known. The bulk of solution of $\frac{N}{10}$ strength which may be made by the iodine present may then be calculated as follows :

Let x = weight of iodine.

Then, since $\frac{N}{10}$ solution contains $12 \cdot 65$ grms. per litre, the required bulk of solution will be $\dfrac{x \times 1000 \text{ c.c.}}{12 \cdot 65}$.

Example.

$$\text{Weight of bottle} + \text{iodine} = 25 \cdot 7050 \text{ grms.}$$
$$\text{,,} \quad \text{bottle only} \quad\quad 18 \cdot 2800 \text{ ,,}$$
$$\text{iodine} = \overline{7 \cdot 4250} \text{ ,,}$$

$$\text{Bulk of solution required} = \frac{7 \cdot 4250 \times 1000}{12 \cdot 6} = 586 \cdot 9 \text{ c.c.}$$

The vessel containing the iodine is now placed, quickly, in a beaker containing a solution of potassium iodide, nearly twice as much of the iodide as there is iodine by weight. The reason for this is that iodine is scarcely soluble in water alone, but appears to form double iodides—tri-iodides (?)—which in the case of the alkali ones are very soluble.

The solution is now transferred to a convenient measuring flask of less than the required bulk of liquid. The beaker is carefully washed with potassium iodide solution, this water all going into the measuring flask, which is finally filled to the mark. The remaining odd cubic centimetres, and fractions, of water required are run into a large, dry beaker from a burette, the contents of the flask is then poured into this beaker, and the whole well mixed by stirring. The flask should be rinsed out with the mixture, and the rinsings poured back. The solution is then ready for use. It must not be exposed to air, but kept in a stoppered bottle.

The above $7 \cdot 425$ grms. of iodine were dissolved in 150 c.c. of water containing about 11 grms. of potassium iodide, and the solution transferred to a 500 c.c. flask. As the final bulk required was $586 \cdot 9$ c.c., 50 c.c. were delivered into a dry beaker from a pipette, and the remaining $36 \cdot 9$ from a burette. The whole was then mixed as described.

N.B.—This iodine solution will keep unchanged for a long time in a stoppered bottle if the bottle be wrapped with brown paper to exclude light or if kept in a cupboard.

PREPARATION OF A DECINORMAL SOLUTION OF SODIUM THIOSULPHATE.

$$\frac{Na_2S_2O_3,5H_2O}{10} = 24 \cdot 8 \text{ grms. per litre.}$$

When iodine reacts with sodium thiosulphate, the equation which represents the reaction is as follows:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$
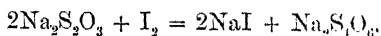
From this it will be seen that only one-half of the sodium reacts with the iodine; hence the weight expressed by $Na_2S_2O_3,5H_2O$ in grms. will be contained in a litre of normal solution, and one-tenth of this amount in a litre of decinormal.

Pure crystals of thiosulphate are powdered and dried by pressing between the folds of blotting paper; $24 \cdot 8$ grms. are then weighed

out accurately, or, as before stated, the proportionate amount of water added, dissolved in water, and the bulk made up to a litre.

Preparation of starch indicator.—About 60 c.c. of water are placed in a large test-tube; as much starch powder as would cover a sixpenny piece is added, and the solution heated and allowed to cool. This indicator should be freshly made each time it is required for a given set of titrations. As is well known, such a starch solution strikes a deep blue colour with iodine, which is destroyed, however, by an excess of sodium thiosulphate. Hence it may be used to determine accurately the end reaction between the two solutions.

TITRATION OF THIOSULPHATE SOLUTION BY IODINE SOLUTION.—25 c.c. of thiosulphate solution prepared as above are placed in a beaker; about 75 c.c. of water and a little starch solution are added. The iodine solution is then run in from a burette until one drop produces a permanent blue colouration, showing the completion of the reaction.

Example (actual).

25 c.c. of thiosulphate solution required 24·8 c.c. of iodine solution

Check 25 c.c. of thiosulphate solution required 24·7 c.c. of iodine solution.

The thiosulphate solution was, therefore, too weak, and was brought to standard strength by evaporating until its bulk was reduced to $\frac{247}{250}$ of the original.* It was then found to be correct.

The converse of this titration, *i.e.*, running the thiosulphate solution into the iodine, is conducted by adding the former until the iodine solution has only a faint yellow tinge, then adding the starch indicator, and running in the thiosulphate solution, drop by drop, until the colour is just discharged. The solutions must be agitated.

PREPARATION OF A STANDARD SOLUTION OF SILVER NITRATE.—The reaction between silver nitrate and soluble chlorides may be represented as follows: $AgNO_3 + NaCl = AgCl + NaNO_3$. For most analyses silver nitrate is usually made into a solution of such strength that 1 c.c. is the equivalent of 0·001 grm. of chlorine, such solution being found most convenient for the titrations in which the salt is employed. As 108 grms. of silver combine with

35·5 of chlorine, it follows that $\frac{108}{35·5} = 3·042$ grms. will combine with

1 grm. of chlorine. If, therefore, a solution be made so that 1 litre contains 3·042 grms. of silver, every c.c. would be the equivalent of 0·001 grm. of chlorine. The solution may be prepared by weighing out this quantity of silver and treating with nitric acid; but it is much more convenient in practice to use the prepared salt, silver nitrate, 4·788 grms. of which contains 3·042 grms. of silver.

* It is best to evaporate a little too much and again titrate. Standing in an open dish in a dry place will often be sufficient.

4·788 grms. of the salt are weighed out accurately and dissolved in water, or a quantity weighed and the calculated amount of water added, as previously mentioned, and the bulk made up to 1 litre. The solution is thoroughly mixed in the usual way, and is then ready for use. It should be standardised by transferring 50 c.c. to a beaker by the aid of a pipette, precipitating with HCl, and weighing. The precipitate should weigh 0·2021 grm. (as may be calculated) ; and the solution should be weakened or strengthened as in the previous cases, according as the precipitate weighs more or less than the above amount.

Silver nitrate may be used for titrations in two ways : first, by using potassium chromate as an indicator, in which case the solution must be *neutral ;* secondly, by observing the point when no further precipitation is caused in the liquid undergoing titration. An example of each of the above methods is given in illustration.

Estimation of chlorine in ordinary water.—100 c.c. of the sample of water are placed in a beaker, and three or four drops of potassium chromate, K_2CrO_4, solution added. The silver nitrate solution is then run in from a burette at the rate of two drops per second, until a distinct red tinge appears in the liquid. A reading is now taken, and another 100 c.c. of the water submitted to titration, care being taken, as in the previous estimations, to run in the last few drops carefully, so that the end of the reaction may be exactly determined. Any indefiniteness in the colour may be obviated by adding a little salt solution to the contents of the beaker in which the first rough titration has been performed and stirring, when the red colour will disappear, and the solution may be used for comparison with the one undergoing the more accurate titration. When one drop of the silver nitrate solution produces a deeper tint than that possessed by the standard, the reaction is completed. Extremely accurate titrations may be made in this manner.

The action of the indicator depends upon the fact that in a solution containing chlorides and a chromate the red silver chromate does not precipitate until the whole of the chlorine present has combined to form silver chloride.

Example.

100 c.c. of well water required 42·4 c.c. of standard silver nitrate solution.

Check 100 c.c. required 42·3 c.c.

Since 1 c.c. of standard silver nitrate = ·001 grm. of chlorine, there was 0·0423 grm. of chlorine present in 100 c.c. of solution = 42·3 parts per 100,000. This sample was contaminated by sewage.

Solutions of brine or sea-water may be titrated by the above method, and will form useful exercises for the student.

Estimation of chlorine in common salt or soluble chlorides by precipitation method.—Weigh out about 0·08 grm. of the dried specimen, and

transfer to a stoppered bottle of about 200 c.c. capacity. Dissolve in about 100 c.c. of water, and add the silver nitrate solution 1 c.c. at a time, placing the stopper in the bottle and shaking well after the addition of each c.c. The precipitate of silver chloride formed will by this means speedily settle to the bottom of the bottle, leaving the liquid clear. This process is repeated until a given c.c. of liquid reagent ceases to produce a cloud in the solution, when the reaction has been completed. A second estimation is now made, running in the whole amount previously used, less $2\frac{1}{2}$ c.c., at one operation. The silver nitrate is now added drop by drop, shaking between each drop again being resorted to, until a given drop is seen to produce no precipitate, when the reading of the burette may be taken.

By preparing a standard solution of common salt equal in strength to the silver nitrate solution (an operation the student should now be able to perform), the reverse of the above process may be used, and the amount of silver in a solution estimated by running in the standard salt solution. An excellent exercise for this purpose is to estimate the silver in a silver coin, by dissolving a weighed quantity in nitric acid, and adding the standard salt solution in precisely the same way as the silver nitrate is used in the precipitation process. A convenient quantity of the coin to take for the purpose is about 0·1 grm.; or about ·5 grm. of the coin may be dissolved in nitric acid in a beaker, the solution transferred to a 250 c.c. flask, and water added to the mark. After mixing, 50 c.c. may be withdrawn with a pipette for titration, and the result checked by repeating the process on another 50 c.c. of the solution.

Any doubt as to whether the reagent has been added in excess may be decided by adding the converse reagent drop by drop. The first drop should produce a slight precipitate, the second *nil*. If the end reaction has been considerably exceeded the amount of converse reagent required to react with the excess must be deducted from the amount of solution used.

Example.

·5 grm. of a silver-copper alloy was dissolved in about 5 c.c. of strong HNO_3, the solution and washings transferred to a measuring flask and diluted to 250 c.c.

50 c.c. of this solution was transferred by a pipette to a bottle, a little water added, and standard salt solution run in as above described. Since every c.c. of solution contained ·001 grm. of chlorine, the silver equivalent of 1 c.c. would be $\dfrac{·001 \times 108}{35·5} = ·003042$ grm. of silver.

1st, 50 c.c. required 24·0 c.c. of standard salt solution.

2nd, 50 c.c. required 23·8 c.c. of standard salt solution.

Since one-fifth of weighed amount was taken, the silver present in total amount taken $= 23·8 \times ·003042 \times 5 = ·362$ grm.

Or, calculated as a percentage, $\dfrac{0·362 \times 100}{·5} = 72·4$ per cent. of silver in alloy.

PREPARATION OF A DECINORMAL SOLUTION OF POTAS-SIUM DICHROMATE.—$K_2Cr_2O_7 = 295 = 3$ atoms = 48 available oxygen, equivalent to 6H, or $\dfrac{295}{60} = 4\cdot915$ grms. per litre.

When potassium dichromate reacts on a ferrous salt in the presence of an acid, the latter is oxidised to the ferric state, as may be expressed by the following equation :

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O.$$
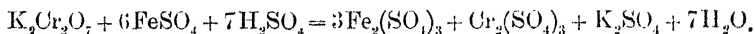
As in the case of the permanganate solution, the amount of salt required must be calculated from the amount of available oxygen in the salt. The molecule $K_2Cr_2O_7$ contains three available atoms of oxygen; and as oxygen is divalent, a normal solution would be represented by the weight $\dfrac{K_2Cr_2O_7}{3 \times 2}$ per litre, and a decinormal by $\dfrac{K_2Cr_2O_7}{60} = 4\cdot915$ grms. per litre. The decinormal solution of this salt is found to be the most convenient strength in practice. To prepare the solution a quantity of potassium dichromate crystals are just melted in a porcelain crucible, so as to completely expel water. It is removed from the crucible, crushed and powdered, and $4\cdot915$ grms. weighed out carefully (or as before mentioned). The weighed quantity is then dissolved in water in a beaker, the contents and washings poured into a litre flask and water added to the mark. After mixing in the usual way the solution may be standardised as follows :

About $0\cdot2$ grm. of clean, annealed iron wire (approximately $99\cdot7$ per cent. of iron) are placed in a flask of about 150 c.c. capacity and 50 c.c. of dilute sulphuric acid poured in from a measuring cylinder. A watch glass of slightly larger diameter than the rim is placed over the flask, which is then warmed until the whole of the metal has dissolved. The solution is immediately poured into a beaker, the flask washed with boiled distilled water and the washings added, and the bichromate solution run in from a burette. The colour of the bichromate turns from yellow to green on entering the liquid, but the end reaction is not visible in the solution. An indicator is found, however, in potassium ferricyanide, which gives a deep blue colour with a ferrous salt, but no such colour with a ferric salt. The ferricyanide, however, must not be introduced into the liquid undergoing titration, but a freshly prepared solution spotted over the surface of a white tile or on a filter paper, and after each addition of bichromate a drop of the liquid is removed by a glass rod and allowed to fall on a spot of ferricyanide. As soon as a given drop of the solution ceases to cause a blue colour in the indicator, the reaction is complete, all the ferrous salt being completely converted into ferric. The last 2 c.c. of solution should, as usual, be run in cautiously, drop by drop, and the liquid tested after each addition.

Example.

0·212 grm. of pianoforte wire was dissolved and titrated as above described, and required 37·7 c.c. of bichromate solution.

Iron actually present in sample $= ·212 \times ·997 = ·2113$ grm.

Therefore 1 c.c. of solution $= \dfrac{·2113}{37·7} = 0·0056$ grm. of iron.

The solution was therefore decinormal.

Estimation of amount of iron in iron ores, &c.—The previous description of the treatment of the iron solution in standardising the bichromate solution will suffice to show how these estimations may be performed when a standard solution of bichromate is at hand. The result may be checked by titrating another sample with the $\frac{N}{10}$ potassium permanganate, the preparation of which has been described. It is advisable to heat the acid strongly in dissolving pig iron, as the carbon present may otherwise form compounds which vitiate the result.

In the case of iron ores, where hydrochloric acid is used to dissolve the compound, the use of permanganate is inadmissible; the bichromate, however, succeeds equally well in this case as when sulphuric acid is employed. When the iron in ferric compounds is to be estimated, the solution must be reduced to the ferrous state by metallic zinc or sulphur dioxide.

It should be remembered that in all titrations in which permanganate or dichromate are employed the acid present takes a part in the process, and should be present to such an extent as to render the solution about normal (N) in acid strength.

SILICON in metals.—Cast irons sometimes contain a considerable amount of silicon. When these irons are dissolved in an acid, as HCl, most of the silicon becomes oxidised to a hydroxide of Si, but in some cases silicon itself may be separated along with graphitic carbon.

Before commencing the analysis of a cast iron for silicon and carbon some idea of the approximate amount present is generally to be obtained. Weigh from 2 to 5 grms. of the iron in the form of fine turnings into a beaker, cover with a clock glass and add N.HCl in quantities of about 10 c.c. at once and at intervals as the action slackens; warm gently. When the action has nearly ceased add 5 c.c. N.HNO$_3$ and 10 to 20 c.c. of 5N. H$_2$SO$_4$ and heat on a steam or sand bath until nearly all the liquid has evaporated. This will take some time. All the HCl and water will go off, leaving a moderately concentrated sulphuric solution. This will completely dehydrate the hydrate of silicon, or silica. Now add about 5 c.c. strong HCl, warm gently, and then dilute with hot water. The object is to get all the iron into solution as chloride and sulphate.

Filter off the black residue, which consists mainly of graphitic carbon and silica, SiO$_2$.

Wash thoroughly with hot dilute HCl and then hot water, place the wet, but drained, filter paper in a platinum crucible and ignite

for some time in the muffle or over the blowpipe. The residue should be nearly white. If still grey or black some graphitic carbon may still be present. Sometimes this may be burnt off by heating the crucible and blowing in a very gentle stream of oxygen from the oxygen bottle. As a rule, however, the carbon burns off completely after heating for some time in the muffle with a good air draught. It is possible to get a good idea of the amount of graphitic carbon by first igniting gently over a Bunsen flame so as to burn off the filter paper, weighing the silica + carbon, then heating in oxygen and weighing again.

The amount of *carbon* in cast iron or steel can be best ascertained by burning or oxidising the metal and its contained carbon. The
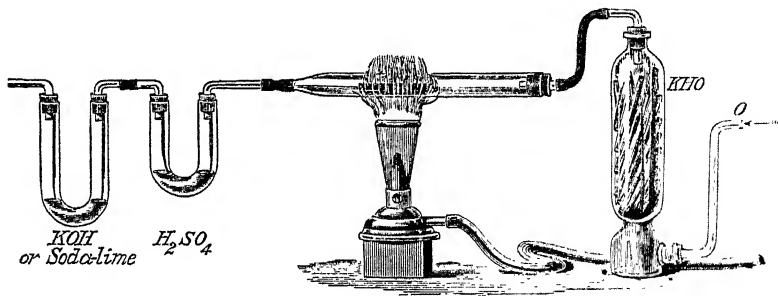

FIG. 43.

carbon will form CO_2, which can be absorbed in KHO or in soda-lime, as in the case of organic substances (see p. 110).

Very little apparatus is needed for this analysis. A supply of oxygen, a combustion tube about 12 ins. long and $\frac{3}{8}$ or $\frac{1}{2}$ in. diameter, a drying and absorbing arrangement, a porcelain boat, or, better, a boat made of thin sheet copper.

The cast iron must be in fine turnings or filings. Weigh the boat, which should be carried in the test-tube carrier, half fill with the iron, and weigh again. Now cover the iron with as much pure dry lead bichromate as the boat will hold, pressing it down tightly and cleanly on the iron. Arrange the U tubes as in Fig. 43 (only the KOH, or soda-lime, tubes are weighed), insert the boat, and allow a gentle stream of oxygen to flow through. Then heat up the tube under the boat, at first with a large Bunsen flame until the lead chromate melts, and then, if possible, assist with a large blowpipe flame. The iron should glow brightly quite through. The end can be seen pretty distinctly, as when the iron and carbon are fully oxidised the contents of the boat cease to glow or appear any hotter than the glass tube. Allow the oxygen to pass through for at least ten minutes after this. Detach the CO_2 absorption tube, cool for a little time, and weigh. CO_2 contains $\frac{3}{11}$ of its weight of carbon. Therefore $\frac{3}{11}$ of the gain in weight of the absorption tube × 100/weight of substance = carbon per cent.

SULPHUR.—Hydrogen sulphide is liberated not only when sulphides, as FeS or Sb_2S_3, are dissolved in acids, as HCl, but also when some metals, as iron, &c., which contain sulphur in some form, possibly as dissolved or combined sulphides (?), are acted upon by acids o that hydrogen is generated.

Cast irons generally contain some sulphur, and when these irons are dissolved in HCl the sulphur escapes with the hydrogen, mainly as SH_2. This gas, on coming in contact with bromine and water or alkaline permanganate solution, is oxidised, the sulphur forming sulphuric acid, which can then be converted into barium sulphate.
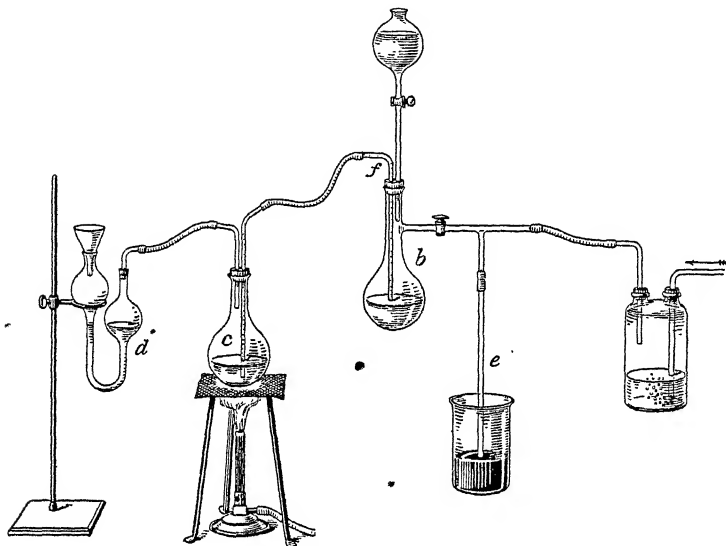

FIG. 44.

The amount of sulphur in irons and other metals is generally small. The apparatus (Fig. 44), in which the metal can be dissolved and any evolved sulphur compound caught, almost explains itself.

Several grams of the substance are weighed into c. The flask b must at first be empty and dry, and a current of hydrogen sent through the whole apparatus so as to expel air. Then acid is let into b from the stop funnel so that the hydrogen drives some liquid HCl over into the substance flask, a little at a time, which can be regulated by the tap. The tube f slides easily through the cork of the. flask. The gas should not pass quicker than two or three bubbles per second through d, which contains bromine dissolved in HCl, in which it is more soluble than in water alone. When all the substance is dissolved a gentle heat may be applied to c, and the gas thoroughly expelled by the hydrogen current. Any excess pressure of hydrogen is regulated by the escape tube e, which dips into half

an inch of mercury or a few inches of water. *a* contains sodium hydroxide solution to absorb any sulphur from the hydrogen used.

After the action is complete the contents of *d* are washed out into a beaker and the H_2SO_4 precipitated by $BaCl_2$, and treated as under H_2SO_4, or barium.

Sulphides may sometimes be treated in this manner. If a weighed quantity of a sulphide, as PbS, be mixed with zinc in the flask *c* the sulphur is more completely and quickly removed as SH_2. Only very small quantities need to be taken for this method.

Many other methods are in use besides this one for the estimation of sulphur in irons and steels, &c. As this book is not intended to instruct on special technical details, but mainly on principles, they cannot be introduced. If an iron or steel is dissolved in dilute nitric acid to which a little bromine water, sufficient to colour it faintly, is added, any contained sulphide is oxidised into sulphuric acid, which may be precipitated by barium salt as usual. Weigh from 2 to 5 grms. of the steel, and dissolve in N. nitric acid in a large flask. The acid may be diluted with bromine water, or the latter allowed to drop into the flask as the action is proceeding. When all is dissolved the solution is diluted to at least 500 c.c., filtered hot, and then kept boiling whilst the barium solution is being added and until the barium sulphate settles out.

The danger lies in the coprecipitation of iron salts. Another plan is to dissolve in the least possible quantity of N. nitric acid, evaporate to complete dryness, whereby most of the ferric nitrate is decomposed, add 1 or 2 grms. of sodium peroxide, then water *very* carefully, and after the violent action has ceased dilute, boil, filter, acidulate with HCl, and precipitate with $BaCl_2$ as before. Great care is required in using the sodium peroxide, as it reacts violently with water and may crack the flask or spirt out substance.

PHOSPHORUS is present in most pig irons, and also in very small quantities in steels, in some phosphor-bronzes, &c.

Special methods are sometimes used for the estimation of this substance.

• For pig or cast iron one method is to dissolve a few grams of the turnings (2 to 10, according to the probable amount of phosphorus) in N. nitric acid, adding the acid only in small quantities at a time and warming until solution is obtained. It is then evaporated to dryness, on a water bath, to make any silica insoluble, redissolved in hot dilute nitric, filtered, and to the clear warm filtrate a solution of ammonium molybdate, containing excess of ammonium hydroxide, added until there is a thick red precipitate and the odour of ammonia is evident. Strong nitric (1·2 sp. gr.) is now added until all the red precipitate is redissolved and the solution is strongly acid. A yellow, very finely divided precipitate will appear. It is ammonium phospho-molybdate. The liquid should be kept warm (80° C.) for some hours to allow the substance to form and completely settle. It may then be filtered off and washed with very dilute nitric acid, in which it is quite insoluble. It may be dried at 100° C. and weighed, the filter paper having been

previously dried and weighed, but if in large quantity is best dissolved from the filter paper by warm ammonium hydroxide. When magnesium chloride, or sulphate, is added to this ammoniacal solution, magnesium ammonium phosphate is formed, and must then be treated as under magnesium or phosphoric acid as described *ante*, p. 74.

Manganese is nearly always present in irons, and nickel in some steels and other alloys.

These metals may be separated as follows: Several grams of the iron are dissolved in HCl. After solution small quantities of nitric acid are added to convert the salt into ferric chloride. Large excess of either acid must be avoided.

The ferric solution is then diluted and placed in a large porcelain dish and *nearly* neutralised with sodium hydroxide or carbonate. No permanent precipitate must be left. It is raised to the boiling temperature, and a solution of sodium acetate added, and the boiling continued until a copious red precipitate has formed and the odour of acetic acid is apparent in the escaping steam. It is now quickly filtered through a folded paper. The filtrate must be absolutely colourless, unless nickel is present in some quantity, and clear. It contains the manganese and nickel, all the iron having formed an insoluble *basic salt*—half acetate, half hydroxide of iron.

To this clear filtrate bromine water is to be added until the whole appears yellow, and then a few c.c. N. sodium hydroxide solution. The temperature of the liquid should be about $60°-80°C$. A black precipitate of the peroxides of manganese or nickel gradually forms. The liquid should stay in a warm place for a few hours.

If either one only of the two metals mentioned is present the precipitate is to be well washed and ignited. The manganese becomes Mn_2O_3 and the nickel NiO. If both are present they may be ignited together and afterwards separated by another operation. This is the case with nickel steel, but cast irons contain only manganese.

NITROGEN.—This element exists in several very distinct forms of combination—for instance, with metals as nitrides, amines, nitrates, and nitrites, and with carbon and organic complexes as cyanides, amines, nitro, azo, and possibly other forms.

Nitrates and nitrites, whether of metals or organic complexes, are all decomposable by strong sulphuric acid. Organic compounds of whatever nature can be so oxidised as to separate the nitrogen in a free state.

The amount of nitrogen in nitrates and nitrites, whether mineral or organic, is most easily and quickly ascertained by the *nitrometer* method, which depends essentially on the reduction of HNO_3 or HNO_2 to nitric oxide, NO, by mercury. In this method a nitrate or nitrite of a metal or an organic group is decomposed by strong sulphuric acid in contact with much mercury, so that the liberated HNO_3 acts at once on the metal.

For instance, $2(KNO_3) + H_2SO_4 = K_2SO_4 + 2HNO_3$ and the liberated HNO_3 then commences to act on the mercury in this sense,

$$8HNO_3 + 3Hg = 3HgN_2O_6 + 4H_2O + 2NO ;$$
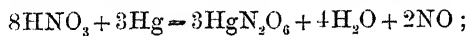
but of course the HgN_2O_6 does not exist for long in the presence of excess of the strong H_2SO_4, but becomes $HgSO_4$ and HNO_3, the liberated nitric acid commencing another course of decomposition.

The instrument is a graduated tube (a in Fig. 45), of 50 or 100 c.c. capacity, with a two-holed stopcock. The lower end is joined by stout rubber tube to b, which is not graduated and should be wider than the measuring tube. The measuring tube is filled to the stopper with mercury, which, however, should only stand at about d in the tube b. The holes in the stopcock should be at least 3 mm. in diameter. The two tubes can be held in any convenient stand, or suspended by a strong cord, the ends fastened to each tube and passing over a bar or hook in a shelf or other support.
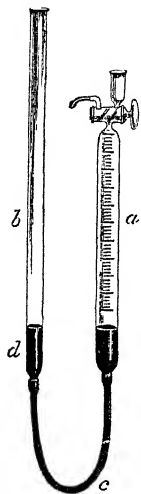

FIG. 45.

To use, fill with mercury, as above, and have the cup at top of a dry. Take about ·03 grm. KNO_3 for the first experiment. Introduce the nitrate and then 2 c.c. of strong H_2SO_4. Turn the tap quickly so that *nearly all* the acid and the nitrate swimming in it enters the tube ; then add another 2 c.c. of acid and admit similarly so that it takes the remainder of nitrate with it. Repeat the addition of smaller quantities of acid three or four times so as to wash all the nitrate into the tube. This operation should be done as quickly as possible, but the *greatest care* must be taken not to let any air in. Another plan more generally used is to weigh the substance in a stoppered bottle, cover with a few c.c. of strong sulphuric, and allow to stand in a cool place until all is dissolved. The solution is then poured into the nitrometer and washed out of the bottle with more acid. This is the better plan, and answers with most nitrates, mineral or organic. Now put a cork loosely in the cup, take a from its support, holding by the cup and stopper with one hand and by the point of junction with the rubber tube with the other, and shake briskly, by a rapid sideways motion. The acid *must never come as low as the rubber junction.* After shaking an action will be visible and gas will collect. Shake at intervals of five minutes until no more gas bubbles appear and the acid becomes clear.

Measure the length of the acid column on the top of the mercury, which is easiest done by counting the divisions it covers on the tube. Now bring tube b close alongside so that the top of the mercury is level with *one-seventh* of the height of the acid column.* Do not handle the gas tube, but clamp or hang them both up. Suspend a thermometer close to the tube for twenty minutes, and read off the number of c.c. of gas. One litre NO weighs 1·3417 grms. (nearly) ; therefore 1 c.c. = ·001342, and of this $\frac{7}{15}$ is nitrogen, since

* Strong sulphuric, being nearly twice as heavy as water, is about one-seventh as heavy as mercury.

$NO = 14 + 16 = 30$. Barometer and temperature must be read off, but there is no correction for moisture, as the H_2SO_4 keeps the gas dry.

If V = observed volume of gas,
$\quad$ P = $\quad$,, $\quad$ pressure,
$\quad$ $t°$ = $\quad$,, $\quad$ temperature,
$\quad$ a = coefficient of expansion = ·003667,
$\quad$ V' = corrected volume,

then

$$V' = V \frac{P}{760 (1 + at°)}, \text{ or } \frac{V . B . 100 . ·001342 . 15}{S . 760 . (1 + ·003667 . t°) . 30} = N \text{ per cent.}$$

1 c.c. NO at NT and $P = ·001342$ grm. and is equivalent to ·00282 HNO_3, ·000627 N, and ·00452 KNO_3. 1 c.c. N at NT and P weighs ·001246 grm.

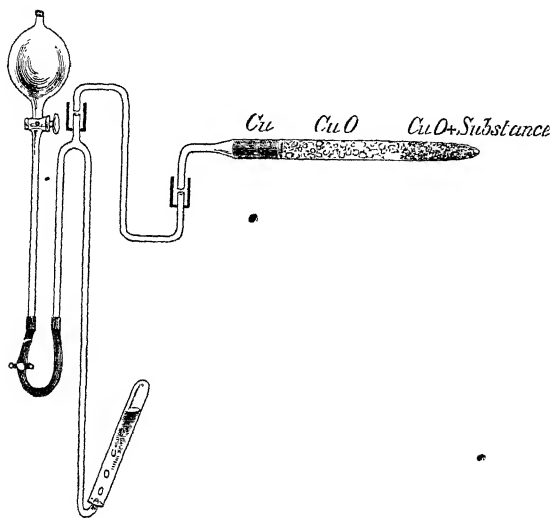Cu $\quad$ CuO $\quad$ CuO+Substance

FIG. 46.

A general method of estimating nitrogen, applicable to all kinds of nitrogen compounds (provided they are not very explosive), is to burn them, by means of the oxygen in copper oxide, CuO, in a vacuum tube, and catch the liberated nitrogen gas in a measuring tube. For this a Sprengel mercury pump is indispensable.

The substance is weighed from a bottle on to a piece of copper foil or into a mortar and mixed with CuO in moderately fine powder. This mixture is then introduced into a piece of combustion tube about 12 ins. long, closed at one end. The mortar or piece of copper is washed by small quantities of granular oxide of copper until the tube is three-fourths filled with this granular oxide. This

must be well shaken down to the closed end, and then a plug of copper made by rolling up copper foil into a cylinder just large enough to enter the tube, inserted. The cylinder should be about 2 ins. long. The tube is now drawn off so as to fit the Sprengel pump tube. (See Fig. 46.)

The pump is set in action and the tube evacuated, the portion of the tube containing the copper foil cylinder being at the same time heated to redness. After a complete vacuum is obtained, as indicated by the mercury falling with a "click" and a column of mercury about 30 ins. high standing in the "fall" tube of the pump, the gas-collecting tube is half filled with strong KHO solution and half with mercury and inverted over the pump end. The pump is stopped and the heat extended backwards to the portion containing the CuO, and, when this is red hot, to the portion containing the substance and copper oxide. Water and gases will now come off. When the whole tube has been thoroughly red hot for ten minutes and gases cease to escape into the collecting tube the pump is again set in action until a vacuum is obtained.

The tube is now removed, by putting a small crucible under the open end, and transferred to a tall cylinder full of water. The strong alkali solution and any mercury fall out and become replaced by water. The tube is held so that the water inside and out is level, and the number of c.c. read off, along with the temperature of the water and the atmospheric pressure.

As the collected nitrogen is measured over water, the tension of water vapour at the temperature must be deducted from the barometer reading.

$w =$ this tension of water vapour. It is $= 9 \cdot 2$ mm. at $10° C.$ and $12 \cdot 7$ at $15° C.$

$$\frac{V \cdot (B - w) \cdot \cdot 001246 \cdot 100}{S \cdot 760 \cdot (1 + \cdot 00366 \, t°)} = N \text{ per cent}$$

Where $V =$ volume of gas,
       $B - w =$ barometer reading minus water vapour pressure,
       $\cdot 001246 =$ weight of 1 c.c. N,
       $S =$ substance, weight taken,
       $760 =$ normal barometer,
$\cdot 00366$ or ∞ coefficient of expansion of gases.

Another method of ascertaining the amount of nitrogen in a substance depends on the fact that most nitrogenous substances when heated with soda-lime (a mixture of CaO with NaHO) yield the whole of the nitrogen in combination with hydrogen as ammonia. This applies strictly to all compounds where the nitrogen is *not* directly united with oxygen.

Nitrates and nitro-derivatives, where the nitrogen is more or less "oxidised," require a considerable modification of this treatment.

Nitro-compounds, as picric acid, $C_6H_2(NO_2)_3OH$, and some amino

and imino compounds, are best analysed by combustion with CuO in a vacuum tube as just described.

The same treatment is necessary with some other classes of nitrogen compounds, but modifications are necessary in some cases. Where the substance is an explosive, for instance, picric acid, mentioned above, would need to be mixed with either fine sand or starch to modify its " decomposition " sufficiently to be safe.

When the nitrogen is determined as ammonia, the operation can be conducted in a piece of " combustion " tube 14–18 ins. long and open at both ends, and so arranged that a stream of hydrogen can be continuously passed through. The tube is heated in a furnace. The hydrogen requires to be washed by passing through water, or a
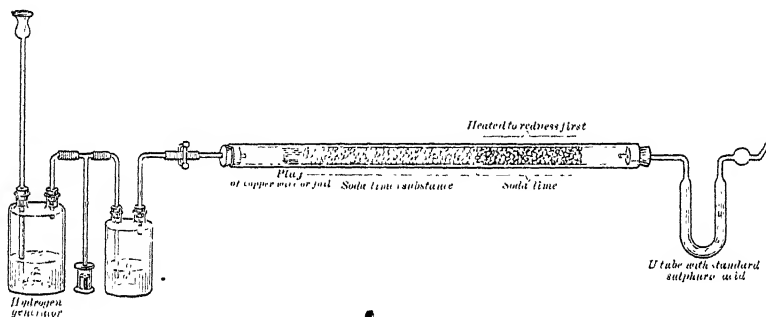

FIG. 47.

potassium hydroxide solution, but need not be dried. More than one absorption tube is desirable.

The figure explains arrangement of tube and charge.

The substance, if a solid, is weighed in a weighing bottle, a small quantity, about ·5 to 1 grm., shaken out into a small dish or mortar, and the bottle weighed again. The quantity shaken out is then mixed by means of a wire with a few grams of dry but cold soda-lime, and by means of a smooth paper gutter introduced into the tube, as will be evident from Fig. 47. There is a plug of copper wire or foil in the front of the tube ; then a layer of about two inches of soda-lime only. The mixture of substance and soda-lime comes after this. The dish or mortar is washed out by more soda-lime, until the tube is nearly full. An excess cannot hurt. Another copper wire, or asbestos plug, keeps the soda-lime in place at one end. This end of the tube has a moderate-sized U tube fitted to it, with cork. The U tube contains a quantity of either H_2SO_4 or HCl of known strength (standard acid).

The ammonia produced in the tube neutralises *some* of the acid. The strength and quantity of acid being known beforehand, the amount actually neutralised by the ammonia can easily be found. The hydrogen is permitted to flow slowly through the tube during the whole time of heating, so as to convey the ammonia as fast as formed into the acid.

After charging the combustion tube with the substance and soda-lime, the U tube, to be fixed at the end, is charged with an accurately known quantity of the acid, and then attached.

After the heating is ended the acid is carefully emptied and washed from the U tube into a dish, a few drops of litmus added, and then the soda solution as with the process of matching it with the acid (see "Acid and Alkali"). If, say, 25 c.c. of $\frac{N}{10}$ acid had been employed in the tube and it required only 20 c.c. of the soda solution for neutralisation, then the difference, 5 c.c., must have
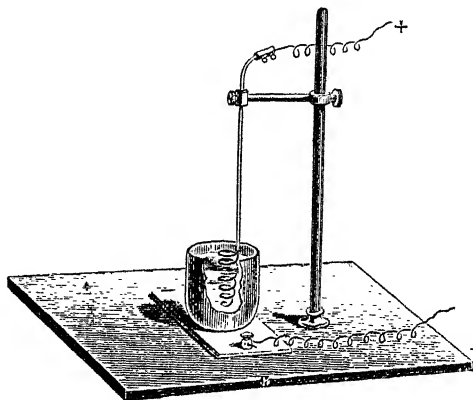

FIG. 48.

been neutralised by the ammonia liberated in the heated soda-lime tube.

With a solution of $\frac{N}{10}$ strength each c.c. = ·0049 sulphuric acid, or ·0017 NH_3, or ·0014 N. So that in the case imagined the amount of nitrogen would be 5 × ·0014, evolved in the form of ammonia.

ELECTROLYSIS.—A number of salts may be decomposed by an electric current and the contained metal deposited in such form that it can be weighed without much difficulty.

One of the easiest substances to experiment with is copper sulphate in solution in water.

Fig. 48 shows one arrangement. The salt should be weighed in a platinum dish or crucible and dissolved in a small amount of water, to which a few drops of sulphuric acid may be added. The current enters by the spiral of platinum wire, and on the stand is a piece of clean metal, brass, copper, or platinum, to which the return wire is connected. Two storage cells giving about 4 volts provide quite enough current; the slower the metal is deposited the more coherent it is.

When the solution has become decolourised, test by taking a very small drop, with a rod, on to a plate or white filter paper and adding a drop of potassium ferro-cyanide solution. When no appreciable

brown coloration is visible, pour the solution carefully into a white dish to see that no particles of metal are carried away, and wash several times, by decantation, with alcohol; dry rapidly in the steam oven till the alcohol has evaporated, and weigh.

If too strong a current be employed the metal is liable to come down in powder, and this oxidises very rapidly during the drying.

Almost any soluble copper or silver salt electrolyses well, but some metals, as nickel, require an alkali salt, as ammonium or potassium oxalate or sulphate, to be present in order to take up the liberated SO_4 "ion."

Nickel or zinc sulphate may be similarly decomposed, and the metals deposited and weighed, provided some *alkali* sulphate is contained in the solution. When copper sulphate is electrolysed as above in platinum the end result may be represented by

$$^-Cu/SO_4^+ + H_2O = H_2SO_4 + O.$$
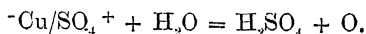
When an alkali salt is present it probably acts as a double salt, thus: $NiSO_4,K_2SO_4$, breaking up on electrolysis in the aqueous solution into $Ni + 2KHSO_4$.

Sulphates are the most convenient salts for electrolysis. From chlorides there is a liberation of chlorine, which attacks even a platinum electrode, and from nitrates oxides of nitrogen, which interfere with the result.

CARBON AND HYDROGEN.—Compounds of carbon and hydrogen require somewhat special methods and apparatus for their quantitative analysis.

The method generally employed is to burn the compound in an excess of oxygen or air in such manner that all the carbon dioxide and water produced can be caught separately and weighed. All the so-called organic compounds contain carbon, and in addition hydrogen, and often oxygen, nitrogen, and other elements.

As carbon dioxide contains carbon to the extent of 12 parts in 44, and water 2 parts of hydrogen in 18, the weights of C and H corresponding to the CO_2 and H_2O can readily be found.

The actual operation is carried out in a glass tube, through which purified, dry air or oxygen can be drawn. In this tube a weighed amount of the substance is heated, and " completely " burnt.

The substance, if a solid, or a liquid of not very volatile nature, may be contained in a " boat " of platinum or of porcelain. If very volatile, then a special tube must be employed.

The actual requisites are:

I. A " tube furnace," which may be simply a row of Bunsen burners (20–30), mounted in a frame, so that a tube of 24–30 ins. length can be heated to redness. If the laboratory be supplied with such furnace no figure is required. Without one the ordinary " combustion " analysis cannot be done.

II. A glass tube about $\frac{5}{8}$ in. clear diameter, and about 4 ins. longer than the furnace. It must be of difficultly fusible glass.

III. An air-aspirator of some kind. A Bunsen waterfall pump is convenient. The simplest is a two- or three-gallon bottle or jar, with an opening near the bottom fitted with a tap. A cork with small tube is fitted to the neck. When the bottle is filled with water, and the tap opened, air is aspirated or drawn in through the top tube to take the place of the escaping water.

IV. A drying and purifying arrangement for the air before it enters the tube. The simplest and most effective consists of a tube about 20 ins. long and about 1 in. diameter, with corks and small tubes at each end, and charged with coarse soda-lime. The air is drawn through this first, and then bubbles through concentrated sulphuric acid contained in a small two-necked bottle. Small glass and rubber tubes are used for connections. From the sulphuric acid bottle the air passes into (V.) the combustion tube. This should
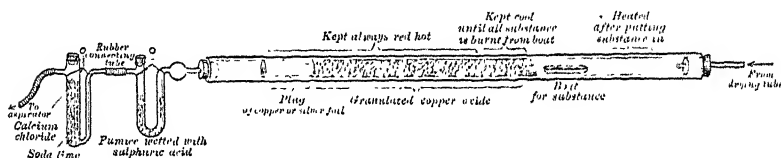

FIG. 49.

be charged with copper oxide, as shown (Fig. 49). It must be "granular" oxide, made from bits of wire.

VI. The absorbing apparatus is first attached directly to the combustion tube—a **U** tube charged with pumice-stone moistened with strong sulphuric acid. This absorbs water only.

2nd. A similar tube, with dry soda-lime, or, better, a tube as seen in Fig. 49, made from a test-tube, and charged, the bottom three-quarters with soda-lime, and the top quarter with dried calcium chloride, just separated by a thin plug of cotton-wool. Two of these tubes should be arranged in series.

The end of this tube is attached by rubber tube with a small **U** tube containing H_2SO_4, to serve as indicator, and then to the aspirator arrangement.

The tubes are weighed separately, and then attached to the tube as shown. The boat is then weighed, the substance introduced, and weighed again. It is usual to carry the boat in a small corked tube; or, better, fit one test-tube into another (see Fig. 12), so that one tube acts as a cap to the opening of the other. The boat and contents are thus protected from loss or gain in transit from the balance to the tube. The tubes are only for carrying the boat, and are *not* put into the combustion tube and not necessarily on the balance pan.

After the substance and boat are introduced the burners *behind* the boat are lit, and as the heat reaches the substance it should gradually either distil into the portion of copper oxide kept cool, or decompose and slowly burn.

Considerable judgment is necessary in conducting this operation.

Some substances may be heated up much more quickly than others, and no rule can be laid down, excepting that a volatile substance must have more time and less heat applied behind the boat at the commencement. There is no particular sign when a combustion is ended and the CO_2 and H_2O swept completely from the tube. It is therefore customary to continue the process for some time after all the substance has gone from boat and tube, and allow time for mixing and sweeping out of the gases. A non-volatile substance may be completely burnt in one hour, whilst a somewhat volatile one may take two to three hours. The time is always less when oxygen is employed.

After the substance has burnt from the boat, and the whole tube has been heated to redness, the tube may be finally cooled by turning off the burners at the end where the air enters and as far as the main bulk of copper oxide. When the combustion appears over, the two tubes, in which water and carbonic oxide have been collected, are separately detached and weighed.

If the drying and purifying apparatus for the air be in proper order, no harm will result from keeping on the operation long after the combustion is really complete, but generally speaking an hour and a half is sufficient.

The weight of substance taken should have some connection, if possible, with its carbon contents, as it is advisable to have a good margin of excess of soda-lime over the CO_2 to be absorbed. From ·2 to ·5 grm. substance is mostly sufficient. As an example, actual:

·1250 substance:

$$\text{gave } H_2O = \cdot 0748.$$
$$CO_2 = \cdot 3887.$$

$$\frac{\cdot 0748 \times 100}{9 \times \cdot 1250} = 6\cdot 65 \text{ per cent. H.}$$

$$\frac{\cdot 3887 \times 3 \times 100}{11 \times \cdot 1250} = 84\cdot 8 \text{ per cent. C, and } 8\cdot 64 \text{ per cent. O by difference.}$$

These figures, on dividing by the atomic weights of each, give a formula $C_{13}H_{12}O$, for which the calculated percentages of hydrogen and carbon are H 6·58 and C 84·78 respectively.

In most compounds oxygen is still "taken by difference." That is, all the other elements are actually found, and the difference from 100 taken as the amount of oxygen, if that element is found by qualitative examination to be present.

A method of combustion in hydrogen has been proposed, but for most cases it is quite unnecessary to have a direct determination of the oxygen, there being no doubt, from other evidence, of its presence.

CARBONATES.—Carbon is also present in carbonates, in which case it is generally liberated as carbon dioxide by the action of some acid, as HCl or HNO_3. The gas may then be absorbed in some alkali, or directly measured in some form of nitrometer tube.

The amount of combined carbon dioxide can also be estimated by "loss"—that is, when a carbonate is treated with a weighed quantity of acid, and the CO_2 only is permitted to escape and the remaining salt weighed.

Schrœtter's apparatus is the most elegant for this purpose, but an apparatus to serve the same purpose can most easily be constructed from a small flask or wide-mouthed weighing bottle, a glass tube with stopper and bulb, and a drawn-out test-tube (see Fig. 50).
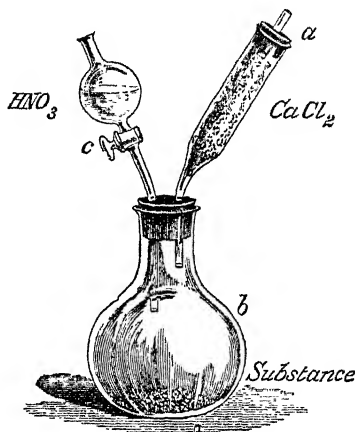

FIG. 50.

The small bulb is charged with HNO_3 or HCl, half acid, half water, the drawn-out test-tube with small pieces of dry calcium chloride. It should be a rubber stopper. The whole apparatus is weighed, and then 1 to 2 grms. of the carbonate placed in the flask and weighed again. The acid is now allowed to flow very gradually into the flask; CO_2 is evolved and is dried by the calcium chloride before escaping. Towards the end the flask is gently warmed, and a slow current of (dry) air drawn through for a few minutes only to remove the CO_2 still in the flask and tube. This can be done by attaching a tube at a to draw by, and another at c, the latter being connected to a **U** tube containing $CaCl_2$ or H_2SO_4. The loss of weight at the third weighing $= CO_2$.
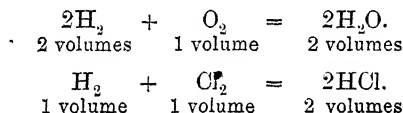
Very small quantities of carbon can also be burnt in a vacuum tube, as with nitrogen (see *ante*, Fig. 46), and measured as CO_2 gas.

CHAPTER VIII.

MOLECULAR WEIGHT.

ACCORDING to Avogadro's hypothesis, "equal volumes of all gases at the same temperature and pressure contain the same number of molecules."

Supposing oxygen, hydrogen, and chlorine, as types of simple elements, to consist of two atoms per molecule, the formation of water and hydrochloric acid, the two most typical molecules, can be shown by the equations:

$$\underset{\text{2 volumes}}{2H_2} + \underset{\text{1 volume}}{O_2} = \underset{\text{2 volumes}}{2H_2O.}$$

$$\underset{\text{1 volume}}{H_2} + \underset{\text{1 volume}}{Cl_2} = \underset{\text{2 volumes}}{2HCl.}$$

The molecules of oxygen have, then, divided so as to be able to join with the hydrogen atoms. The number of water molecules is twice that of the oxygen molecules, but equal to the number of hydrogen molecules; but as the volume of steam produced is double that of the oxygen there must be in equal volumes as many water molecules as oxygen molecules and hydrogen molecules.

Avogadro's hypothesis suggests a means of (1) ascertaining the relative weight of gaseous molecules, (2) forming an idea as to the number of atoms in a molecule.

If now equal volumes of gases contain the same number of mole-cules, the ratio of the weights of these volumes gives the *molecular weights*.

If the relative weight of steam be 9, based on hydrogen as unity, and hydrochloric acid 18·25, the ratio of the molecular weights of water and hydrochloric acid is 9 : 18·25.

VICTOR MEYER'S METHOD.—The apparatus for this method is very simple (see Fig. 51). In the tube A the weighed quantity of substance is vapourised, and the vapour displaces its own volume of air, which escapes by the side tube and is collected in C, where it is measured, and, after reduction to standard temperature and pressure, its weight calculated. The weight of substance, divided by this weight of air, evidently gives the relative weight to air. The air

8

may even be supposed to be hydrogen, because hydrogen and air occupy the *same volume* by Avogadro's law.

In this process the substance to be vapourised is weighed in a tiny tube (to be seen inside the bulb of A), the quantity taken being such that the air displaced by its vapour can all be collected in the 50 c.c. measuring tube. In the outer tube B is a liquid of higher boiling-point than that of the substance to be examined. The substance must, of course, be able to withstand the temperature necessary for complete vapourisation without decomposition or change. The cork is removed from A, the liquid boiled in B, and the tube C, filled with water, adjusted over the end of A. The heating is kept up until the whole system has come into a steady state of gain and
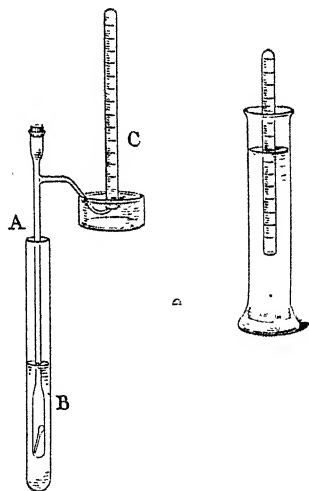

FIG. 51.

loss of heat. This may be twenty or thirty minutes. (A cotton-wool or asbestos plug at the top of B is an advantage.) The small tube, with its contained substance, is then dropped in open end foremost, and the cork, quite leisurely, placed in A. No air must be pushed into C during this corking. In the course of a minute or two the substance in the little tube will begin to vapourise, and the vapour rising in the tube will push its own volume of air before it into C. The action may begin slowly and then become quite violent, ceasing again suddenly. When no more bubbles escape—generally two or three minutes—the cork is removed from A, the measuring tube carefully transferred to the cylinder full of water, the water made level inside and outside the tube, and the volume read off, temperature and pressure being at the same time noted.

$$D = \frac{S \times 760 \times (1 + \cdot00367t°)}{V \times (B - w) \cdot00008896}.$$

D = density.

S = weight of substance.

V = volume of collected air (or hydrogen).

(B − w) = the height of barometer, less the pressure of water vapour at temperature of observation.

760 = normal height of barometer.

·00367 = coefficient of expansion of gases.

·0000896 = weight of 1 c.c. hydrogen.

DETERMINATION OF MOLECULAR WEIGHTS— CRYOSCOPIC AND EBULLIOSCOPIC METHODS.

The determination of the molecular weight of a substance by the cryoscopic or ebullioscopic method depends upon two facts which have long been well known, but which have only comparatively recently been so thoroughly investigated as to render these methods of molecular weight determination of at least equal importance to the older method of determination depending upon the density of the substance in the gaseous state. The new methods of determination have the further advantage that they can be applied to all soluble substances, and not merely to those which are volatile without decomposition.

CRYOSCOPIC METHOD.—The cryoscopic or freezing-point method depends upon the well-known fact that the solution of any substance in a given medium lowers the freezing- (or melting-) point of that medium. Thus it is well known that salt water freezes with much greater difficulty than fresh water, and that a saturated solution of common salt in water is more difficult to freeze than sea water itself.

This brings out the first point in connection with the determination of molecular weight by the cryoscopic method—viz., that the depression of the freezing-point of any solvent is directly proportioned to the quantity of matter of any one kind dissolved in it.

Dealing with matter of various kinds, it is found that equal weights of different substances dissolved in the same weight of solvent usually produce differences in the depression of the freezing-point of the solvent. Thus it is found that in the cases of the chlorides of potassium and sodium dissolved in water, 74·5 parts by weight of potassium chloride lower the freezing-point of water to the same extent as 58·5 parts of sodium chloride in the same amount of the same solvent. These numbers 74·5 and 58·5 are, for certain reasons, considered to be the molecular weights of KCl and NaCl respectively, and hence 74·5 parts of KCl and 58·5 parts of NaCl contain an equal number of molecules, from which it follows that the depression of the freezing-point of a solvent depends upon the number of molecules of substance dissolved in it, and that an equal number of molecules of all substances have the same effect in lowering the freezing-point of the solvent.

The actual determination of the molecular weight by this process is carried out as follows : A suitable solvent having been selected, a weighed quantity is taken and its freezing-point accurately determined by means of a special thermometer graduated to $\frac{1}{100}$°, and by which the temperature can be estimated to $\frac{1}{1000}$° C. The special thermometer is so constructed that a portion of the mercury can be transferred to another bulb at the top of the thermometer, and in this way, by altering the amount of mercury used, the thermometer
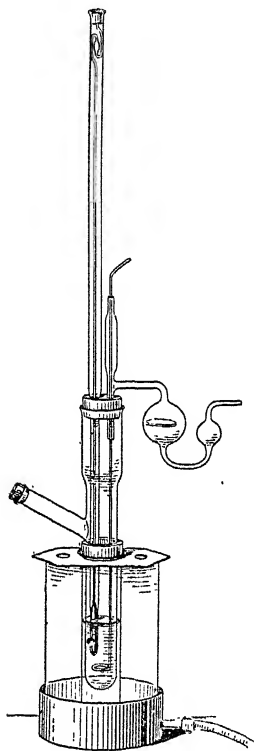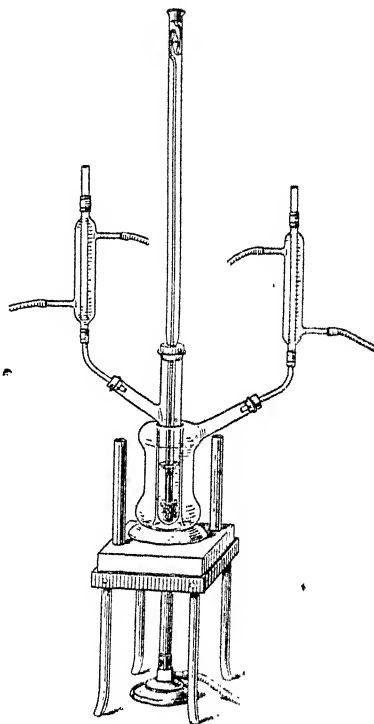

FIG. 52.   FIG. 53.

can be made available for use over a wide range of temperature, and therefore with various solvents.

It should be remembered that the absolute freezing-point of the solvent is not required in the determination, but that the method consists in determining the difference between the freezing-point of the pure solvent and the freezing-point of the solvent containing a known weight of substance in solution. The thermometer is therefore so adjusted that the freezing-point of the solvent falls well within the scale of the thermometer. The solvent is then cooled, with constant stirring, to a temperature somewhat below its freezing-point

(nearly all substances undergo superfusion* and can be cooled more or less below their true freezing-point without solidifying). Suddenly solidification begins to take place and the temperature begins to rise. The highest point to which the temperature rises is taken as being the true freezing-point of the solvent. This point should be determined two or three times or till a constant result is obtained. When the freezing-point of the weighed amount of solvent has been determined, a weighed amount of the pure dry substance of which the molecular weight has to be determined is dissolved in the liquid, and the freezing-point is again determined as before. The difference between the two freezing-points gives the depression. The solution should not, as a rule, be a strong one; 2 to 3 per cent. is usually sufficient to give a sufficiently well-marked depression in the freezing-point, except in the case of substances possessing a very large molecular weight.

The molecular weight may now be easily calculated by means of the following formula :

$$\text{M.W.} = C \times \frac{W}{D} \times \frac{100}{S} \; :$$

where M.W. = molecular weight,
   W = weight of anhydrous substance (in grams),
 D (or $\delta t°C$) = depression of freezing-point in degrees C.,
   S = weight of solvent taken (in grams).

 * *Superfusion.*—The melting-point of a solid is a most characteristic property of the substance, not only as regards temperature, but also the potential heat of melting. The action of heat on a solid, causing it to rise in

Boiling Point
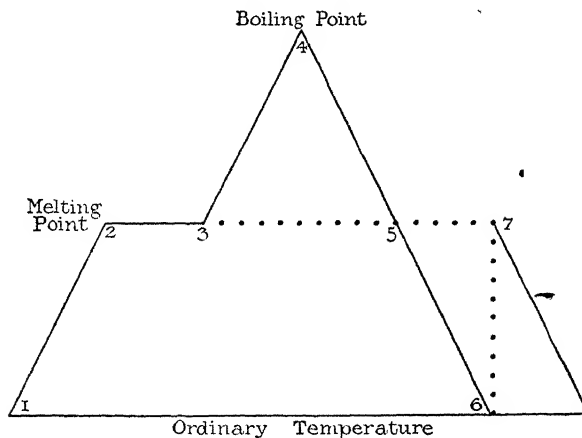
Melting
Point

Ordinary Temperature
FIG. 54.

temperature (expand also, perhaps), melt, and finally vapourise, can be shown by the rough diagram. At 1 the substance is solid; at 2 begins to melt, and absorbs heat-energy to a certain extent until all is melted at 3, remaining all this time at the melting temperature; it then gets hotter until 4, the boiling-point.

C is a number which has to be introduced according to the solvent selected for the determination. It is a number which is a constant for each particular solvent. It may (if unknown) have to be determined by finding the depression produced in the freezing-point by weighed quantities of substances of known molecular weight, as determined, say by the Victor Meyer Method, when in the above equation all the terms will be known except C, which can then be easily calculated.

The values of C for the solvents most generally used, together with the approximate freezing-points, are appended.

	F.P.	C.		F.P.	C.
Ethylene bromide	8	118	Aniline	6	58·7
Acetic acid	17	39	Nitro-phenol (1 : 2)	41	71·1
Benzene	5	49	β-Naphthol	121	112·5
Xylene (1 : 4)	16	43	Tribromo-phenol		
Naphthalene	80	68	(2 : 4 : 6)	95	201
Anthracene	213	116·5	Water	0	18·5
Phenol	38·5	74	Nitro-benzene	6	70

The idea of the cryoscopic method of molecular weight determination is chiefly due to the chemist Raoult. The special thermometers and the practical process and apparatus are the invention of Beckmann.

EBULLIOSCOPIC METHOD.—The ebullioscopic method of molecular weight determination is similar in principle to the cryoscopic method, but depends upon the elevation of the boiling-point of a solvent produced by the solution of a given weight of the substance of which the molecular weight has to be determined.

The thermometer used is similar to the one for cryoscopic determinations, and the apparatus generally used has been designed also by Beckmann. This apparatus consists of two parts—an inner one in which the actual boiling-point determinations are made, and an outer one in which the same liquid (or one of nearly the same boiling-point) is heated with the object of screening the inner portion from draughts and so obtaining perfectly constant temperatures. Both portions have a condensing arrangement to prevent loss of liquid. The boiling-point of a weighed portion of the solvent is first determined to $\frac{1}{1000}°$, and then a weighed quantity of the substance is introduced and the elevation of the boiling-point determined. (As before, absolute temperature measurements are not required.) The point at which the boiling liquid becomes constant in temperature is taken in both cases, and the difference gives the elevation of the boiling-point. The bulb of the thermometer must be completely

is reached. On carefully reversing the process from the boiling-point it is easily possible to pass the point 5, where the substance should solidify and *give up* its potential heat of melting. and the whole be cooled down to ordinary temperature, but remain a liquid. In this condition, on being *touched* with some of the same substance in a solid state, this liquid will suddenly solidify, the potential energy then appearing as heat, the same amount being produced as was absorbed in the stage 2–3. The temperature will therefore rise from the ordinary to 7, which by the diagram is evidently equal to 2, or the melting-point.

immersed in the boiling liquid, and in order to render the boiling regular it is usual to introduce a quantity of some solid substance which is not acted upon or dissolved by the liquid.

The molecular weight can be calculated from the following formula :

$$\mathrm{M.W.} = \mathrm{C} \times \frac{\mathrm{W}}{\mathrm{E}} \times \frac{100}{\mathrm{S}} \, ;$$

where M.W. = molecular weight,
      W = weight of anhydrous substance (in grams),
      E = elevation of boiling-point in degrees C.,
      S = weight of solvent.

E is more generally put as Δt°.

C is a number or constant depending upon the solvent used.

Values of C and approximate boiling-points of different liquids :

	B.P.	C.		B.P.	C.
Carbon bisulphide .	46	23·7	Water . . .	100	5·2
Carbon tetrachloride .	78	48	Ethylic acetate . .	75	27
Chloroform . .	61	36·6	Benzene . . .	80	27
Ethylene dibromide .	132	63·2	Nitro-benzene .	205	50·2
Eethylic alcohol .	67	9·0	Aniline . . .	184	32·2
Mthylic alcohol . .	79	11·5	Phenol . . .	183	30·4
Ether . . .	35	21	Camphor . . .	204	61
Acetone . . .	56	17	Pyridine . .	115	30
Formic acid . .	101	34			

The illustrations will give a much clearer notion of the apparatus used than any description. It is not necessary to use a chemically pure solvent in either method to obtain satisfactory results, but naturally the use of impure solvents is to be deprecated.

WITH THEIR RESPECTIVE GROUP REAGENTS.

Group I. Hydrochloric Acid.	Group II. Sulphuretted Hydrogen, in acid solutions. N.B.—Nitric acid should be absent.	Group III. Ammonium Chloride, Ammonium Sulphide, and Hydroxide.	Group IV. Ammonium Chloride, Carbonate, and Hydroxide.	Group V. (No characteristic group reagent.)
Lead . as $PbCl_2$.* Silver . ,, AgCl. Mercury,, Hg_2Cl_2.†	Mercury . . . as HgS, black. Lead . . . ,, PbS,‡ ,, Bismuth . . ,, Bi_2S_3, ,, Copper . . ,, CuS, ,, Cadmium . . ,, CdS, yellow. Tin(Stannosum),, SnS, brown. Tin (Stannicum),, SnS_2, yellow. Antimony . . ,, Sb_2S_3, orange. Arsenic . . ,, As_2S_3, yellow. Gold . . ,, Au_2S_3, black. Platinum . . ,, PtS_2, ,,	(1) *Hydroxides.* Aluminium as $Al_2(HO_6)$, white. Chromium ,, $Cr_2(HO_6)$, green. (2) *Sulphides.* Iron . . . as FeS, black. Zinc . . ,, ZnS, white. Manganese ,, MnS, buff.§ Nickel . . ,, NiS, black. Cobalt . . ,, CoS, ,, (3) Phosphates, Arsenates, Borates, Silicates, Fluorides, &c., of metals other than the alkalies.	Barium as $BaCO_3$. Strontium ,, $SrCO_3$. Calcium ,, $CaCO_3$.	*In solution :* Magnesium. Potassium. Sodium. Ammonium.

* When no colour is stated, the precipitate is white. There are degrees of whiteness, however, depending on the physical condition, density, crystalline form, &c., of the precipitate.

† Precipitated as mercurous chloride from mercurous salts.

‡ Lead chloride, $PbCl_2$, being somewhat soluble even in cold water, lead is found both in the first and second group.

§ Varies in colour, depending on concentration and temperature of solutions.

N.B.—Most of the so-called rare metals can be "placed" in these groups, but are omitted here for simplicity.

CHAPTER IX.

ANALYTICAL GROUPS: REACTIONS OF THE METALS OF GROUP V.

THIS group comprises the metals potassium, sodium (alkali metals), ammonium, and magnesium, which are not precipitated by any group reagent, as most of their compounds are very soluble in water.

(1) **POTASSIUM**, K. Atomic weight, 39·1. Specific gravity, 0·87. Melting-point, 62·5° C. Boiling-point, 719-731° C.—Is found in combination in large amount only in a few minerals, of which salt-petre is the most important. It is present in some silicates, such as felspar, in the ashes of plants (crude potashes), and in the form of chloride in saline deposits (at Stassfurth in Germany and elsewhere).

The metal is obtained by driving the melted hydroxide over very strongly heated iron turnings, and condensing the vapour in a heavy mineral oil, petroleum, which has no action upon it, and also protects it from the air. It has a brilliant silver-white lustre on a freshly cut surface, which immediately tarnishes on contact with air, becoming covered with oxide. It decomposes water when brought in contact with it, the heat produced being sufficient to inflame the liberated hydrogen. The metal is so soft that it may be easily squeezed by gently pressing a small piece with the end of a test-tube or glass rod. It is generally kept under rock oil or paraffin, to prevent oxidation.

N.B. *Caution.*—Do not on any account touch the metal with the fingers or bring it in contact with acids.

Experiments.
• I. A *very* small piece, not larger than a pea, of the metal is taken from the petroleum, dried between several thicknesses of dry blotting-paper, and placed on a porcelain crucible lid and gently warmed.

The metal will melt and then ignite in the air. White fumes escape, and a greyish substance, mostly K_2O, remains on the lid. Allow to cool, then place in water. The greyish oxide will dissolve and the temperature will rise considerably. Great care must be taken that all the metal has oxidised, or an explosion may result.

The water will be found to convert red litmus into blue. Reserve this solution.

II. Carefully wipe as before a very small piece, less than in I., of the metal, and drop on to some perfectly clean and cold water contained in a dish covered by a funnel, as in Fig. 55.
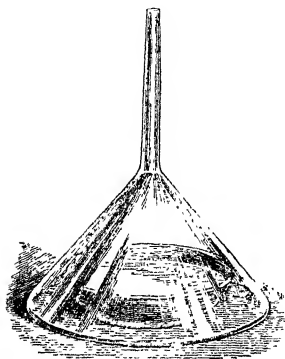
A beaker covered by a funnel will do as well. The metal will appear to burn. The flame is really due to hydrogen, but it is coloured by some potassium vapour. A red-hot globule of potassium oxide swims on the water, and finally dissolves with a slight explosion.

Test this solution as in I. Then add a diluted acid drop by drop until litmus paper shows neither red nor blue, but a claret tint. A salt of potassium has been formed. Evaporate the solution to dryness, when crystals of the salt will be left.

FIG. 55.

Dry Reactions of Potassium Compounds.*

Most potassium compounds, heated in small quantities on a thin platinum wire in the inner flame of the blowpipe, or in the lower outer edge of the Bunsen flame, undergo dissociation, the vapour of the metal imparting a violet colour to the outer flame. When examined with the aid of a spectroscope † the potassium spectrum is found to

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* When solids are heated in a tube, or on charcoal, or on a platinum wire, without any liquid being employed on them, they are said to be undergoing "**dry**" reactions, or the dry examination.

These dry reactions are given, as a rule, by every compound of the element.

When dissolved in water or other solvent, and this solution is treated with reagents, it is undergoing "**wet**" tests, or reactions in solution.

As regards wet reactions, almost any soluble compound of the element will answer. Some do so in an eminent degree, and are also easy to obtain. Nitrates, chlorides, sulphates, are, generally speaking, most workable in this respect, and should be used in doing the reactions. Oxides, sulphides, phosphides, and insoluble compounds are less suitable, as they sometimes complicate matters for beginners by producing secondary reactions or complex products.

N.B.—Students are advised to perform all the experiments and reactions with each metal of a group, and then attempt a method of separation founded on the knowledge gained. Use the salts you have made from the metal, if possible, for the first reactions.

† When elements in the gaseous condition, or vapourised by strong ignition, are examined by means of the spectroscope, they may be distinguished from each other by the respective spectra which they give. The intensity of the spectra of metallic elements is so much greater than that of the non-metals that the latter are only rarely seen. The heat which can be produced by a good Bunsen gas-burner is not strong enough to volatilise all elements or to heat their vapour highly enough. Most heavy metals can only be volatilised by means of an electric spark, making use of an induction-coil, by placing

consist mainly of two lines, a comparatively strong line, Ka,* in the red, and a faint line, Kβ, in the blue.

This applies more particularly to those potassium salts which are volatile without decomposition at a strong red heat (such as potassium chloride, bromide, iodide, and cyanide) or which are decomposed by heat; but not to non-volatile potassium salts, such as phosphates, silicates, or borates, which give scarcely any flame reaction until they are moistened with an acid, as hydrochloric, or, if that be without action, heated together with pure calcium sulphate or silver sulphate. The presence of sodium compounds gives rise to an intense golden-yellow flame, which conceals the potassium reaction; but when seen through a blue glass, or indigo solution, the yellow or sodium flame is entirely cut off, and the potassium flame becomes distinctly visible, and is then of a rich reddish-violet colour.

the metals between the poles. In order to analyse the ordinary gases spectroscopically, the spark is passed through the gases, contained in tubes which are filled with the gas and then exhausted with an air-pump. The filling and exhausting is repeated several times, and finally a good vacuum obtained. Traces of the gases are left, which on agitation by an induction spark become luminous. These tubes can be made and used by any one if a Sprengel or other mercury pump is available   (See Fig. 56.)
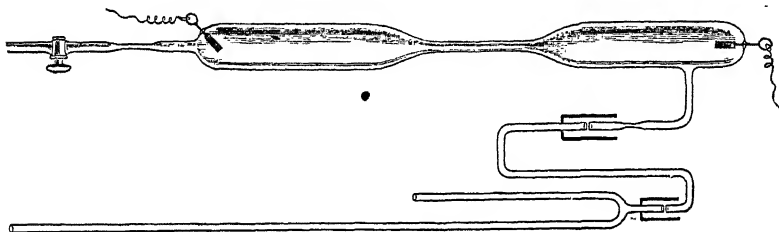

FIG. 56.

It is usual to employ the spectroscope only for the examination of those elements which can be volatilised by means of a gas flame, viz., a good Bunsen burner. Such are the alkali metals, sodium, potassium, rubidium, cæsium, lithium; the alkaline earthy metals, barium, strontium, calcium; and the heavy metals thallium and indium. Lead, copper, arsenic, antimony, and some other metals, and phosphorus, boric acid, and less easily sulphur, selenium, tellurium, will also show colours in a Bunsen flame, and a few lines may be distinguished. The compounds most suitable are the chlorides, nitrates, chlorates, and carbonates of the metals. A small portion is placed on a loop of thin platinum wire, introduced into the non-luminous portion of the flame, and the spectrum of the coloured flame examined. The different elements are distinguishable by their respective colours, as well as by the position which certain coloured lines or bands occupy in the continuous solar spectrum. The lines are not all of the same intensity, and therefore not equally available, so that it is only by employing large quantities of pure substances, and heating them very intensely, that many of the less prominent lines can be observed. The delicacy of the reaction is, however, so great that the merest traces can be discovered. Spectroscopic analysis constitutes a most valuable auxiliary to the ordinary means of chemical investigation.

* Principal spectral lines of elements are generally designated by a letter for ordinary reference purposes. Compare the table of some metallic elements opposite title-page.

A more simple method of detecting potassium in the presence of large quantity of sodium compounds is the following: A small ortion of the substance is moistened with concentrated hydrochloric cid and placed on a loop of thin platinum wire. The wire is then radually brought near to a point in the Bunsen flame about half n inch above the top of the burner. Compounds of potassium eing more volatile than those of sodium, the violet-coloured flame ill be clearly observed before any trace of the yellow sodium flame visible.

eactions in Solution.

Nearly all potassium salts are soluble in water.

Platinic chloride, $PtCl_4$, precipitates from potassium solutions hich are not very dilute, a yellow crystalline precipitate of potas- um platinic chloride, $2KCl.PtCl_4$, insoluble * in strong alcohol, or alcohol and ether mixture, as well as in acids.

$C_2H_2(OH)_2(CO_2H)_2$ (tartaric acid) precipitates white crystalline rdrogen potassium tartrate, $C_2H_2(OH)_2CO_2HCO_2K$, from neutral and fficiently concentrated solutions. The precipitate settles rapidly, pecially after shaking or stirring.

$2HF,SiF_4$ (hydrofluosilicic acid) gives a white gelatinous precipi- te of potassium silicofluoride, $2KF,SiF_4$; difficultly soluble in water in 833 parts at 17·5° C.); insoluble in alcohol.

The hydroxide and carbonate constitute two important reagents, account of the chemical activity of the metal or base potassium, ich can supplant or expel most other metals from their com- nations with acids, &c.

) **SODIUM**, Na'. Atomic weight, 23. Specific gravity, 0·974. elting-point, 96° C.—This metal somewhat resembles potassium in pearance, but is a little harder, and does not oxidise so rapidly in c, nor is its action on water so energetic as that of the latter metal. s compounds occur in nature in vast masses, as rock salt, $NaCl$; carbonate, in native soda, $Na_2CO_3,10OH_2$, and in trona, $a_2CO_3,2HNaCO_3,3OH_2$; as nitrate, in cubic nitre, or Chili saltpetre, aNO_3; as sulphate or Glauber's salt, $Na_2SO_4,10OH_2$; as biborate, $a_2B_4O_7,10OH_2$; as glauberite, $Na_2SO_4,CaSO_4$; and as cryolite, NaF,Al_2F_6; and in many silicates, of which albite may be taken as e representative. Most sodium compounds are easily soluble in ter, a few silicates and cryolite excepted.

Sodium may be obtained in a similar manner to potassium, and o by heating the hydroxide or oxide to a high temperature with rbon. The metal distils over similarly to potassium, and is kept der petroleum or in a perfectly dry atmosphere.

xperiments.

I. A small piece of sodium (freed from oil) heated on a bit of rcelain behaves very like potassium, K, but requires a little higher

* The degree of solubility of a precipitate in different media can only be certained by quantitative experiments.

temperature before commencing to burn. The oxide produced is generally whiter than with K. Its behaviour with water is almost identical with that of K.

II. A small piece of the metal placed in cold water, as with potassium, melts and runs about and disengages hydrogen, which may be set on fire. The flame is coloured intensely yellow. A globule of red-hot hydroxide floats on the water, and finally dissolves, spirting or exploding as it cools down. The solution is alkaline to litmus, as with K.

Neutralise the solution with an acid, and evaporate to dryness. Note the physical characters of the salt produced, whether deliquescent, &c.

N.B.—Sodium should not be touched by the fingers, *and must not be put in contact with acids.*

Dry Reactions.

The intense golden-yellow colour which sodium compounds impart to the outer blowpipe flame is almost exclusively relied upon for the detection of the metal. Its spectrum consists of a bright double line, coinciding with the D line of the solar spectrum, and several green lines, somewhat difficult to see. Some sodium salts are readily recognised by their characteristic taste, especially rock salt and cubic nitre.

Reactions in Solution.

Sodium salts are even more freely soluble in water than potassium salts, and platinic chloride or tartaric acid give no precipitates, although analogous compounds are formed. Hydrofluosilicic acid gives a gelatinous precipitate from concentrated (aqueous) solutions only; the precipitate is insoluble in alcohol.

Sodium hydroxide and carbonate act in many respects like the corresponding potassium compounds.

Both metals form oxides, K_2O and Na_2O, and, in addition, peroxides or dioxides, K_2O_2 and Na_2O_2. Sodium dioxide has become a technical product, and is largely used as an oxidising agent. A little of these is formed when the metals burn in air. Sodium dioxide is made by heating the monoxide, Na_2O, in a current of air or oxygen. These oxides on contact with water become very hot; oxygen is evolved, and some peroxide of hydrogen is also produced.

(3) **AMMONIUM,** NH_4, generally shortened to Am. Combining weight, 18. Hypothetical metal or "compound radical" in combination.

Ammonia, NH_3, is obtainable from nitrates by the action of nascent hydrogen, as when moist iron or zinc filings or aluminium is mixed and heated with a nitrate; from the distillation of many organic compounds, containing nitrogen, with a hydroxide, as KHO. Its chief commercial source at present is coal, the NH_3 being formed during the heating of coal in the gas manufacture. From the coal-gas it is separated by washing with water and weak acids.

Experiments.

Mix a few grams of potassium nitrate with five or six times as much fine iron filings and moisten very slightly. Warm the mixture gently in a test-tube or flask fitted with a cork and glass tube. (See Fig. 22, or " Chlorine," later.)

Catch some of the gas in an inverted dry test-tube in which a piece of red litmus paper has been placed. Fill another tube similarly and then introduce a few drops of water ; close tube with thumb and shake. A partial vacuum will be formed by the gas dissolving in the water. Add litmus to the water. Add acid to this water until neutral, and evaporate carefully to dryness—best on a water-bath. An ammonium salt is formed.

The reaction between a nitrate and moist iron may probably be shown by the two expressions

$$2(KNO_3) + 5Fe = 5FeO + K_2O + N_2,$$
$$3Fe + 3H_2O = 3FeO + 6H,$$
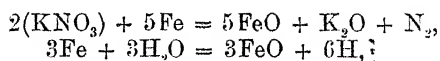
the actions going on simultaneously. The H and N being liberated together, combine to form $2(NH_3)$. The reactions may, however, be more complex than this.

Feathers, horsehair, wool, or silk, cut into small pieces and mixed with two or three times as much calcium hydroxide (slaked lime), in powder, and then heated, also give off ammonia.

Any ammonium compound, as sal ammoniac, NH_4Cl, when mixed and warmed with lime, or almost any other oxide or hydroxide, will give off NH_3 as gas : $2NH_4Cl + CaO = 2NH_3 + H_2O + CaCl_2$.

The gas is very soluble in cold water, but may be expelled therefrom on boiling for a short time. Alcohol dissolves still more NH_3 than water. Both solutions absorb CO_2 from the air.

When ammonia, NH_3, either in the gaseous state or in solution in water, comes in contact with acids, a " direct " combination takes place. No hydrogen is displaced on either side ; thus, $NH_3 + HCl = NH_4Cl$. The water solution of NH_3 acts very much like KHO or $NaHO$, and is therefore termed a hydrate or hydroxide, supposed to be NH_4OH. The salts of ammonia closely resemble K and Na salts ; hence the " um " ending, which indicates that in combination NH_3 appears to some extent to act the part of a metal.

A red-hot platinum wire suspended in a mixture of ammonia gas and air continues to glow owing to an oxidation of the hydrogen and nitrogen. Some oxides of nitrogen are formed, which eventually, on contact with water, produce a mixture of nitric and nitrous acids. NH_3 does not burn in air, but readily in oxygen, with a yellow flame. Ammonia solution slowly oxidises on exposure to air, some nitrous acid being formed.

Some metals, as Na, K, Mg, decompose NH_3 when heated in a stream of the gas, giving off hydrogen and forming nitrides :

$Na_2 + 2NH_3 = 2NaNH_2 + H_2$, and $2NH_3 + 3Mg = Mg_3N_2 + 3H_2$.
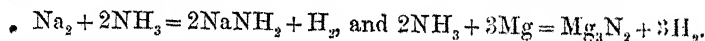
These nitrides are decomposed again by water into metallic oxides

and NH_3 : $Mg_3N_2 + 3H_2O = 3MgO + 2NH_3$. Some of this nitride is formed when Mg burns in air.

Dry Reactions.

Most ammonium salts, when strongly heated in a dry tube, volatilise, either entirely or partially. Salts with non-volatile acids, such as phosphoric, lose ammonia, NH_3. Salts of ammonium with volatile acids can be volatilised, either *with* decomposition, such as the nitrate, nitrite, sulphate, the latter with formation of nitrogen, water, ammonia, and sulphurous anhydride ; or practically unchanged, such as the chloride, bromide, iodide.

When solids vapourise on heating and condense again to solids on the cooler parts of the apparatus the process is termed **"sublimation."** It does not differ essentially from distillation.¶

Reactions in Solution.

All ammonium salts are soluble in water.

Platinic chloride produces a heavy yellow precipitate of ammonium platinic chloride, $2NH_4Cl,PtCl_4$. The precipitate is soluble in much water (hence there appears no precipitate from dilute solutions), but insoluble in alcohol and ether. Ammonium platinic chloride leaves on ignition *only* spongy platinum. (Distinction from potassium platinic chloride, which leaves spongy platinum and potassium chloride, $Pt + 2KCl$.)

Tartaric acid produces from a concentrated solution of an ammonium salt a white crystalline precipitate of hydrogen ammonium tartrate, resembling the potassium precipitate in its appearance. The two precipitates are readily distinguished on ignition. Hydrogen potassium tartrate leaves a carbonaceous residue, which is strongly alkaline, and the potassium carbonate which it contains dissolves in water. The other leaves merely a residue of carbon, devoid of any alkaline reaction.

Neutral or normal salts of some polybasic oxy-acids—*e.g.*, well-dried alkali borates or phosphates—readily decompose ammonium salts, especially when heated, with evolution of ammonia gas and formation of acid salts. Calcium phosphate will also liberate NH_3, thus :

$$Ca_3P_2O_8 + 2NH_4Cl = Ca_2H_2P_2O_8 + CaCl_2 + 2NH_3, \text{ and}$$
$$Ca_2H_2P_2O_8 - H_2O = Ca_2P_2O_7.$$
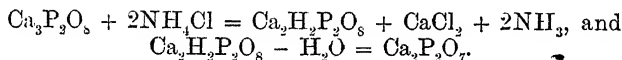
This reaction distinguishes, therefore, between normal and acid salts of polybasic acids.

A number of other phosphates behave similarly to the calcium salt.

Ammonia gas is readily recognised, 1st, by its pungent odour ; 2nd, by its turning red litmus paper blue ; 3rd, by its combining with the vapour of volatile acids (such as hydrochloric acid) to form white fumes (NH_4Cl).

Nessler's test* for traces of ammonia.—If an alkaline solution of

* For the preparation of Nessler's solution, see Appendix (Reagents).

potassium mercuric iodide, $2KI,HgI_2$, be added to a fluid containing mere traces of ammonia or of an ammonium salt, a brown precipitate of dimercurammonium iodide or a yellow to brown coloration is produced, according to the quantity of the ammonium compound present:

$$2(2KI,HgI_2) + 3KHO + NH_4HO = NHg''_2I,OH_2 + 7KI + 3OH_2.$$
$$\text{Brown pp.}$$
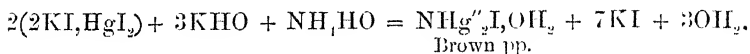
Ammonium salts and nitrates and nitrites, when heated together, react thus:

$$NH_4Cl + KNO_3 = KCl + 2H_2O + N_2O,$$
$$\text{and } KNO_2 + NH_4Cl = KCl + 2H_2O + N_2.$$
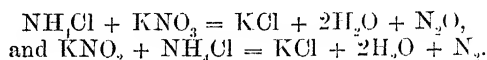
The latter reaction takes place also in aqueous solution.

In consequence it is possible that ammonia may escape detection in a mixture of this kind if the nitrate or nitrite be in excess and the mixture be heated.

This behaviour is the basis of the diazo- reaction (see later), which is of extreme importance in the production of organic dye-stuffs, and also of explosives of a peculiar type.

(4) **MAGNESIUM,** Mg''. Atomic weight, 24. Specific gravity, 1·75. Melting-point, 750° C. Boils at about 1100° C. (?).—This metal is silver-white, malleable and ductile, does not oxidise in dry air, but is readily acted upon by acids, and also decomposes water when boiled with it. It occurs in nature as oxide, in the mineral periclase, MgO; as hydrate in brucite, $Mg(HO)_2$; as carbonate in magnesite, $MgCO_3$; and in hydromagnesite, $3MgCO_3,Mg(OH)_2,3H_2O$; as double carbonate in dolomite, $CaCO_3,MgCO_3$, and mesitine spar, $MgCO_3,FeCO_3$; as sulphate in kieserite, $MgSO_4,H_2O$ (from Stassfurth salt), and in epsomite, $MgSO_4,7H_2O$; as silicate in peridote, Mg_2SiO_4, enstatite, $MgSiO_3$, steatite, $3MgSiO_3,SiO_2$, talc, $4MgSiO_3,SiO_2$, serpentine, $2MgSiO_3,Mg(OH)_2$, and in diopside, $CaSiO_3,MgSiO_3$; and as borate in boracite, $3MgB_2O_4,B_2O_3$.

Magnesium is generally prepared by the action of sodium on the chloride, $MgCl_2$, or double chloride, $MgCl_22NH_4Cl$, or by electrolysis of the magnesium sodium chloride.

Magnesium combines with nitrogen at a red heat, forming Mg_3N_2.

Magnesium may be employed in some cases of reduction of elements, as silicon, boron, &c., from their oxides or chlorides. For instance, the metal (in filings) heated with sand gives silicon and also some magnesium silicide. $2Mg + SiO_2 = 2MgO + Si$, and $4Mg + SiO_2 = SiMg_2 + 2MgO$. (See also CO_2.)

These reactions can be performed in glass tubes or porcelain crucibles.

Experiments.

I. Mg heated in a tube, in contact with air, generally inflames at about the melting-point. A white oxide, MgO, is formed, which is very light, but neither volatile nor fusible; it scarcely dissolves

in water, but placed on moist red litmus paper it just turns it blue
It dissolves in acids.

II. Boiled with water, hydrogen is slowly given off and $MgOH_2O$
formed—a white powder soluble in acids. Burning magnesium
ribbon introduced into steam continues to burn.

III. Heated with sulphur *to a high temperature* in a hard glass
tube, a sulphide can be obtained, but in a test-tube the glass gives
way before this action begins.

IV. HCl acts very energetically, giving off hydrogen and forming
$MgCl_2$. H_2SO_4, dilute, acts similarly, and the solution on evaporation
gives crystals of $MgSO_4,7H_2O$, magnesium sulphate. Nitric acid
acts more slowly; as this solution is evaporated nearly all the nitrate
is decomposed and MgO left.

V. Alkali hydroxides dissolve the metal, forming white MgO and
evolving hydrogen.

VI. The metal, when placed in solutions of salts of zinc, iron,
copper, &c., precipitates these metals as crystalline powders.

Dry Reactions.

Magnesium salts impart no colour to a non-luminous gas-flame.
The most characteristic reaction for magnesia, in the dry way, is the
pale rose colour which this oxide acquires on moistening it with
cobalt nitrate, and then igniting it once more strongly on charcoal.

This colour can, however, only be relied on when no other
metallic oxides are present; recourse must almost invariably be had
to reactions *in* solution. Ignition of the sulphate on charcoal in the
reducing flame yields the sulphide, MgS. Prolonged ignition of the
carbonate yields the oxide, magnesia, MgO, which is almost insoluble
in water. The chloride $MgCl_2$ also loses chlorine on ignition in air.
The nitrate is very easily decomposed, oxide resulting.

Reactions in Solution.

No precipitate is produced in magnesium salts by ammonia in
the presence of ammonium chloride, or other ammonium salts, be-
cause it forms a soluble double salt.* In the absence of ammo-
nium chloride, part of the magnesium is precipitated as hydroxide,
$Mg(HO)_2$, thus:

$$2MgCl_2 + 2NH_4HO = Mg(HO)_2 + 2NH_4Cl,MgCl_2.$$
<div align="center">Soluble double chloride</div>
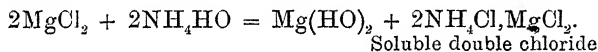
In the presence of a sufficient amount of ammonium chloride the
magnesium hydroxide is at once decomposed into magnesium chloride,

* A number of compounds of this nature exist, but their "constitution" is
not known with certainty, so they are provisionally termed "molecular"
combinations or double salts.

The magnesium-ammonium salt is possibly

$$\begin{array}{ccc} HClNH_2 & & HCl. \\ & \diagdown Mg \diagup & \\ HClNH_2 & & HCl. \end{array}$$

9
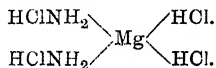
$Mg(HO)_2 + 2NH_4Cl = MgCl_2 + 2NH_4HO$, and no precipitation takes place, nor is the double chloride precipitated by ammonium, sodium, or potassium carbonates, unless the two latter be boiled for some time with the double salt.   Hence magnesium cannot be precipitated in Groups III. and IV., provided a sufficient amount of ammonium chloride be present and the solution be kept moderately dilute.

Potassium, sodium, calcium, and barium hydroxides precipitate magnesium almost completely as white magnesium hydroxide, nearly insoluble in cold and hot water.   Ammonium chloride as well as other ammonium salts dissolve it readily, and, if originally present in sufficient quantities, prevent its formation.

Ammonium oxalate gives after some time from moderately dilute solutions of magnesium salts a white crystalline precipitate of a double oxalate of magnesium and ammonium, but not in the presence of excess of ammonium chloride.   N.B.—In this case excess means very little more than necessary to form the " double " salt.

Hydrogen disodium phosphate precipitates hydrogen magnesium phosphate, $HMgPO_4$.

In the presence of ammonium chloride and ammonium hydroxide ammonium magnesium phosphate, NH_4MgPO_4, is formed as a white crystalline precipitate.   A very dilute solution should be gently heated and stirred with a glass rod.   The precipitate deposits on the faint scratches caused by the glass rod on the tube.   The precipitate is almost insoluble in water and ammonium salts.   In very dilute aqueous ammonia it is practically insoluble.   Dilute mineral acids dissolve it, as also acetic acid.   From very dilute solutions the precipitate separates only on standing for about twenty-four hours in a warm place.

On heating magnesium chloride with precipitated mercuric oxide, the chloride is converted into oxide, mercuric chloride being volatilised.   This experiment must be conducted in a closet which is provided with a good indraught of air, and is in connection with a chimney flue.   Nearly a red heat is required.

Methods for the recognition and separation of Mg, K, Na, and Am will readily suggest themselves, if the student bear in mind :

1st. The volatility of ammonium salts (phosphates and borates excepted).

2nd. The insolubility of $Mg(HO)_2$ in water.

3rd. The insolubility of $2KCl,PtCl_4$ in alcohol.

4th. The intense yellow colouration sodium compounds impart to the blowpipe or Bunsen flame.

A solution containing salts of Mg, K, Na, and NH_3 may be examined as follows :

I. Heat a portion with NaHO ; ammonia gas is given off, which is recognised by its pungent odour and effect on red litmus paper = presence of NH_3.

II. To a second portion add ammonium chloride, ammonium hydroxide, and sodium phosphate ; a white crystalline precipitate indicates the presence of Mg.

III. Evaporate a third portion to dryness and ignite strongly.

Extract with hot water (without filtering off any magnesium oxy-chloride• (Mg_2OCl_2) which may have been formed), and add sufficient $Ba(HO)_2$ till the whole of the magnesium is precipitated as $Mg(HO)_2$; filter. To the filtrate add $(NH_4)_2CO_3$ as long as a precipitate is produced, and filter again. Evaporate the filtrate to dryness, and ignite strongly to expel ammonium salts. Dissolve the residue in a little water, filter off a trace of MgO (if any); and test filtrate for potassium by means of $PtCl_4$,—a yellow crystalline precipitate = presence of K ; and for sodium by heating on a platinum wire in a non-luminous flame—a golden-yellow flame indicates the presence of Na.

It is, however, not necessary to get rid of magnesium before testing for potassium and sodium by the flame reactions or even by $PtCl_4$ for K.

The metals of this group are, chemically speaking, the most energetic elements of the metal class. They are able to turn out or displace most other metals, and some non-metals, from their compounds with oxygen, halogens, or acids.

CHAPTER X.

REACTIONS OF THE METALS OF GROUP IV.

THIS group comprises the metals barium, strontium, and calcium, which are precipitated by ammonium carbonate from an ammoniacal solution in the presence of ammonium chloride. The latter (if present in sufficient quantity) prevents the precipitation of magnesium.

The three elements barium, strontium, and calcium are not well known in the metallic state. They resemble each other very closely in physical and chemical properties, and their compounds are often, indeed generally, found associated in nature.

	Atomic weight.	Sp. gr.	Melting-point.
Ba . .	136·76	3·75	about that of cast iron.
Sr . .	87·39	2·54	at a red heat.
Ca . .	39·91	1·57	at a red heat.

The metals are not sensibly volatile at the highest furnace temperature. They appear to be volatile in the electric furnace. They all decompose water at the ordinary temperature, and oxidise rapidly, on the surface, in air. When heated to redness in air or oxygen they burn very brilliantly.

The oxides of these metals do not fuse or vapourise even in the oxy-hydrogen blowpipe flame, but glow very brightly—become **luminous.**

They are not reduced by carbon in any ordinary furnace. In the "electric furnace" compounds of carbon are formed, termed carbides. They may be represented by the formula $M.C_2$. On contact with water these carbides give an oxide and acetylene :

$$CaC_2 + H_2O = CaO + C_2H_2.$$

The metals may also be made in the electric furnace.

The melted chlorides of these metals on electrolysis, by carbon electrodes, give also the metal and chlorine.

The operation can be performed in a small graphite crucible heated over a good Bunsen flame, using rods of gas carbon to lead in the current from five or six accumulators.

Very small globules of the liberated metals attach themselves to the anode or negative carbon, and may, with difficulty, be obtained by rapidly removing the carbon and dipping into heavy petroleum.

(1) **BARIUM**, Ba''.   Occurs in nature chiefly in the form of heavy spar, $BaSO_4$, and as witherite, $BaCO_3$.

Dry Reactions.

Barium compounds when held in colourless flame or when heated on thin platinum wire in the inner blowpipe flame impart a yellowish-green colour to the outer flame, especially when previously moistened with strong hydrochloric acid.   When viewed through the spectroscope (the chloride or chlorate show best), two green lines, Baα and Baβ, come out most intensely; Baγ is less marked.   Besides these, there are numerous lines in the red and yellow, and one broad, indistinct line in the blue, close to F of the solar spectrum.
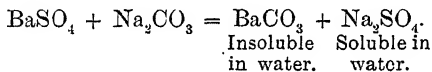
Heavy spar heated on charcoal in the reducing flame is reduced to barium sulphide, BaS, which fuses readily.   This reaction is made use of to prepare on a manufacturing scale soluble barium salts from the sulphate.   Barium carbonate is decomposed only slowly even by ignition to a strong white heat.

Experiment.

Salts should be made from the BaS or $BaCO_3$ for testing.

Reactions in Solution.

Barium salts are obtained by dissolving the native carbonate or witherite $BaCO_3$ in dilute acids.*   Heavy spar is attacked by alkali carbonates at a high temperature.   By mixing, on a small scale, finely powdered barium sulphate with three or four times its weight of fusion mixture or sodium carbonate, and heating in a platinum crucible over a gas flame, it is converted into barium carbonate, thus :

$$BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4.$$
$$\text{Insoluble} \quad \text{Soluble in}$$
$$\text{in water.} \quad \text{water.}$$

On extracting the fused mass with hot water and filtering, $BaCO_3$ is left, which is soluble in most acids.

The nitrate, chloride, chlorate, and acetate are soluble in water. Use dilute solutions.

$(NH_4)_2CO_3$ (group reagent) precipitates white barium carbonate, $BaCO_3$, soluble with decomposition in acids, somewhat soluble in ammonium chloride.   With carbonic acid it forms a soluble acid carbonate $(BaCO_3,H_2CO_3)$, which is reprecipitated on boiling, with evolution of carbon dioxide.   Barium carbonate is partially decomposed by alkali sulphates—e.g., potassium sulphate—into barium sulphate and alkali carbonate.   The decomposition is complete in the presence of free carbon dioxide. $SrCO_3$ and $CaCO_3$ are not changed, even on boiling with K_2SO_4.

Sodium or potassium carbonate, same precipitate.

KHO and NaHO, free from carbonates and sulphates (which they

---

* Dilute acids (HCl or HNO_3) should be employed, as the barium chloride and barium nitrate, which result from the action of these acids upon witherite, are insoluble in the concentrated acids.   Normal acids are strong enough.

rarely are), give from highly concentrated solutions a voluminous precipitate of hydroxide, $Ba(HO)_2$, soluble in water. A solution of this hydroxide in water is known as baryta water. It possesses a strong alkaline reaction and great affinity for carbon dioxide, for which it is used as a reagent.

NH_4HO gives no precipitate.

H_2SO_4, and all soluble sulphates, give on warming, and especially in the presence of free acid, a white, heavy precipitate of barium sulphate, $BaSO_4$, even from excessively dilute solutions of barium salts. The precipitate is insoluble in water, dilute acids, and alkalies; soluble to a perceptible extent in boiling concentrated hydrochloric and nitric acids, and also in concentrated solutions of ammonium salts, but not if the precipitants are in excess; soluble also in concentrated boiling sulphuric acid, with formation of dihydrogen barium disulphate, $BaSO_4,H_2SO_4$. The presence of an alkali citrate greatly interferes with its precipitation. Solutions of strontium or calcium sulphate (two sulphates which are but slightly soluble in water, especially the former) constitute the most characteristic tests for barium.

$BaSO_4$ requires about 400,000 parts of pure water for solution; $SrSO_4$, 7000 parts; whilst $CaSO_4$ dissolves in 390 parts of water at 35° C., and in 460 parts at 100° C., being, in fact, less soluble in hot than in cold water.

Hydrogen disodium phosphate gives from neutral or alkaline solutions a white precipitate of hydrogen barium phosphate, $HBaPO_4$, readily soluble in dilute nitric, hydrochloric, or acetic acid. Perceptibly soluble in ammonium chloride.

$C_2O_4(NH_4)_2$ (ammonium oxalate) gives from a moderately dilute solution of a barium salt a white pulverulent precipitate of barium oxalate, C_2O_4Ba, soluble in dilute nitric or hydrochloric acid. Soluble also, when freshly precipitated, in oxalic and acetic acids.

K_2CrO_4 (potassium chromate) gives a bright lemon-yellow precipitate of barium chromate, $BaCrO_4$, even from very dilute neutral or moderately acid (acetic acid) solutions, readily soluble in nitric, hydrochloric, or chromic acid (H_2CrO_4); reprecipitated by ammonium hydroxide. (Distinction from strontium and calcium salts, which are not precipitated from dilute solutions if acetic acid be present.)

Hydrofluosilicic acid gives a colourless crystalline precipitate of barium silicofluoride, BaF_2SiF_4, which subsides quickly, especially upon the addition of an equal bulk of alcohol. It is somewhat soluble in water and in dilute acids, but insoluble in alcohol. (Distinction of barium from strontium and calcium salts, which give no precipitate even on the addition of alcohol.)

Soluble barium salts constitute exceedingly useful reagents for the detection of several acids, on account of the metal barium forming many insoluble salts.

(2) **STRONTIUM,** Sr″.—Occurs in nature as sulphate in the mineral celestine, $SrSO_4$, and as carbonate in strontianite, $SrCO_3$.

Dry Reactions.

Strontium compounds colour the Bunsen flame intensely crimson. When the flame is viewed through the spectroscope it shows a number of characteristic lines, more especially the $Sr\beta$ and γ lines in the red and the line $Sr\delta$ in the blue, which latter is particularly suited for the detection of strontium in the presence of Ba and Ca.

Celestine, $SrSO_4$, heated on charcoal in the reducing flame, is converted into strontium sulphide, SrS, from which the chloride may be prepared for blowpipe and other reactions by treating the residue with hydrochloric acid. Strontium carbonate, heated in a platinum crucible over a gas blowpipe, is almost completely converted into oxide after about twenty minutes' heating.

Reactions in Solution.

The nitrate, chloride, acetate, are somewhat more soluble than the corresponding barium salts.

$(NH_4)_2CO_3$ (group reagent) gives a white precipitate of strontium carbonate, $SrCO_3$, less soluble in ammonium chloride than the corresponding barium carbonate; soluble in dilute acids. Carbonic acid produces the soluble hydrogen strontium dicarbonate $SrCO_3,H_2CO_3$, which is decomposed on boiling into normal carbonate, carbon dioxide, and water.

Sodium or potassium carbonate, same precipitate.

H_2SO_4, or a soluble sulphate, produces a white precipitate of strontium sulphate, $SrSO_4$. From dilute solutions a precipitate appears only after some time, especially if calcium sulphate be used as the precipitant. Heat assists the precipitation. The precipitate dissolves perceptibly in hydrochloric or nitric acid, but is insoluble in alcohol. It is insoluble also on boiling in a concentrated ammoniacal solution of ammonium sulphate made alkaline with ammonia. (Distinction between strontium and calcium.)

A solution of strontium sulphate in water is not precipitated by ammonium oxalate, but itself readily precipitates barium salts.

Hydrogen disodium phosphate gives a white precipitate of hydrogen strontium phosphate, soluble in acids, including acetic acid.

Ammonium oxalate precipitates strontium salts more readily than barium salts. The white precipitate of strontium oxalate, C_2O_4Sr, is readily soluble in dilute nitric or hydrochloric acid; somewhat soluble in ammonium salts and in oxalic or acetic acid.

The chromate, $SrCrO_4$, is soluble in acetic acid and other acids, nearly insoluble in water and ammonia.

(3) **CALCIUM**, Ca''.—Occurs in enormous quantity in nature, in combination with carbonic, sulphuric, silicic, and phosphoric acids. In plants it occurs combined with carbonic, sulphuric, and phosphoric acids; in animals combined with phosphoric and carbonic acids. It is occasionally also found in minerals which result from the action of acids (such as nitric or arsenic acid) upon calc spar or chalk.

The principal calcium minerals are the various calcium carbonates,

which differ in physical properties or in crystalline structure, such as Iceland spar, generally very pure, $CaCO_3$, calc spar (containing occasionally barium, magnesium, iron, manganese, lead, in variable proportions, and passing gradually into baryto-calcite and dolomite, siderite, diallogite, and plumbo-calcite), arragonite, marble, limestone, chalk; the sulphates, such as gypsum, $CaSO_4, H_2O$, anhydrite, $CaSO_4$, alabaster, selenite; the phosphates, such as apatite, some containing both chlorine and fluorine; bone-earth, $Ca_3P_2O_8$, and fluor spar, CaF_2.

The metal calcium can now be obtained in the electric furnace by reduction of the oxide CaO by carbon. It is a silver-white, soft, malleable metal, which tarnishes rapidly in moist air, but keeps bright in dry air at ordinary temperatures. It combines with nitrogen rather more readily than magnesium at the same temperature, forming a similar nitride. It also decomposes ammonia, forming either an amide, CaNH, or nitride, and decomposes water, forming the hydroxide.

A compound with carbon, CaC_2, or calcium carbide, is formed in the electric furnace from CaO and carbon, which on contact with water gives acetylene, C_2H_2.

Owing to its power of combining with both carbon and nitrogen, it acts as an agent in the production of cyanamide, &c.

Calcium alloys (or unites) with other metals, Cu, Al, Mg, somewhat easily, and, owing to its powerful attraction for oxygen, can be used for reducing metallic oxides or refining metals by taking away dissolved oxides, &c.

Dry Reactions.

Most calcium compounds, when heated in the inner flame of the blowpipe, colour the outer flame yellowish-red; phosphate and borate excepted. The presence of strontium entirely obscures the calcium reaction. The calcium spectrum shows, among other lines in the red and yellow, an intensely green line, $Ca\beta$, also an intensely orange line, $Ca\alpha$.

Calcium carbonate when strongly ignited becomes converted into caustic or quicklime, CaO. It combines with water very eagerly, evolving much heat, and is converted into calcium hydroxide, $Ca(HO)_2$ (slaked lime), which is strongly alkaline. It is less soluble in water than either barium or strontium hydroxide. It is also more soluble in cold than in hot water. Calcium sulphate is converted into calcium sulphide, CaS, when ignited on charcoal in the reducing flame. It also reacts alkaline.

Reactions in Solution.

Calcium salts are readily prepared from pure calc spar or marble, by means of dilute acids. Many of its salts are soluble in water, the nitrate and chloride especially so, and are deliquescent.

$(NH_4)_2CO_3$ (group reagent) precipitates white calcium carbonate, $CaCO_3$, which is bulky and amorphous at first, but on warming gently rapidly becomes crystalline. Calcium carbonate is somewhat soluble in ammonium chloride, especially when freshly pre-

cipitated. It is, in fact, partially reconverted on boiling into calcium chloride.

Sodium or potassium carbonate, same reaction.

H_2SO_4, or a soluble sulphate, precipitates from *concentrated* solutions of a calcium salt white calcium sulphate, $CaSO_4H_2O + Aq$, soluble in much water, and still more soluble in acids. A precipitate is obtained on the addition of twice the volume of alcohol from solutions which are too dilute to be precipitated by sulphuric acid or by a soluble sulphate. Calcium sulphate dissolves readily on boiling in a concentrated solution of ammonium sulphate, especially if slightly alkaline with ammonia.

A solution of calcium sulphate precipitates both barium and strontium salts.

Hydrogen disodium phosphate gives a bulky white precipitate of tricalcium phosphate, $Ca_3P_2O_8$, soluble in dilute hydrochloric or nitric acid, and soluble in acetic acid, especially when freshly precipitated; reprecipitated by ammonium hydroxide.

Potassium chromate gives a precipitate only in strong and neutral or alkaline solutions.

Ammonium oxalate produces even from very dilute solutions of calcium salts a white pulverulent precipitate of calcium oxalate, $C_2O_4Ca + Aq$, readily soluble in hydrochloric or nitric acid; not perceptibly soluble in oxalic or acetic acid. On gentle ignition calcium oxalate breaks up into calcium carbonate and carbon monoxide gas, and on igniting very strongly calcium oxide is left.

Soluble calcium salts, such as the chloride or nitrate, constitute important reagents for the detection of organic acids, more especially dibasic acids, on account of the metal calcium forming insoluble salts with many of them.

SEPARATION OF BARIUM, STRONTIUM, AND CALCIUM.
—Barium minerals frequently contain strontium and calcium, and strontium minerals barium and calcium as well. One method of separating these metals may be based upon :

1st. The insolubility of $BaCl_2$ in absolute alcohol,* $SrCl_2$ and $CaCl_2$ being soluble.

2nd. The insolubility of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ in absolute alcohol, $Ca(NO_3)_2$ being soluble.

For this purpose a hydrochloric acid solution of the mineral containing Ba and Sr or Sr and Ca, or possibly Ba, Sr, and Ca, is prepared, and the solution evaporated to dryness and gently ignited. (Strong ignition must be avoided, as $CaCl_2$ is slightly decomposed into an insoluble basic salt when heated in air—$CaOCaCl_2$.)

Barium is separated from strontium and calcium by digesting the finely divided residue with absolute alcohol, and separating from the undissolved $BaCl_2$ by filtration.

Strontium is separated from calcium by evaporating or distilling off the absolute alcohol, which contains the $SrCl_2$ and $CaCl_2$,

* Methylated spirit that has been dried by standing over some fresh CaO and then distilled—or even filtered will do.

precipitating with ammonium carbonate, filtering, and converting the strontium and calcium carbonates into nitrates by means of dilute nitric acid. The solution of the two nitrates is evaporated to dryness on a water-bath and absolute alcohol added, when calcium nitrate is dissolved out, strontium nitrate being insoluble in absolute alcohol.

Several other methods for recognising and separating the metals of Group IV. will suggest themselves.

It is often necessary to ascertain whether one or two or all the metals of this group are present in a solution. This can be done by adding to their neutral solution a solution of K_2CrO_4, or $2HF,SiF_4$. A yellow or a transparent crystalline precipitate indicates barium. To a portion of the filtrate add $CaSO_4$; a precipitate forms, perhaps only after some time, proving the presence of strontium; or the solution remains clear, in which case calcium only need be looked for, the presence of which is indicated by the precipitate which ammonium oxalate produces from another portion of the largely diluted solution. If both strontium and calcium are present separation is necessary.

No difficulty will be experienced by the student in drawing up schemes of analysis based upon:

1st. The insolubility of $BaCl_2$ and $Sr(NO_3)_2$ in absolute alcohol.

2nd. The insolubility of $BaCl_2$ in absolute alcohol and that of $SrSO_4$ in a concentrated solution of $(NH_4)_2SO_4$.

3rd. The insolubility of BaF_2,SiF_4, or $BaCrO_4$, as well as of $SrSO_4$, in water, $CaSO_4$ being sufficiently soluble to be readily indicated by ammonium oxalate.

4th. A good plan is to make a solution of the three metals in acetic acid, and to add to this potassium chromate. $BaCrO_4$ only is precipitated. The filtrate is now made acid with H_2SO_4, when $SrSO_4$ is precipitated; the filtrate from this, on addition of oxalic acid, or ammonium oxalate, gives another precipitate of CaC_2O_4.

$BaCrO_4$ is yellow, the other two precipitates are white, but the solution may be yellow owing to excess of the potassium chromate.

The same mixture should be examined by all these processes, so as to get an idea of their relative accuracy. Normal solutions will be strong enough to bring out these differences.

CHAPTER XI.

REACTIONS OF THE METALS OF GROUP III., OR THE AMMONIUM SULPHIDE GROUP.

GROUP III. comprises the metals aluminium, chromium, iron, cobalt, nickel, manganese, zinc. The phosphates of these metals, and of magnesium, barium, strontium, and calcium, are also precipitated if phosphoric acid be present.

To get an idea of the working of this group it is advised that some if not all of the following exercises be performed :

1. Add to a centinormal solution containing cobalt nitrate, ferric chloride, and calcium phosphate, dissolved in a little dilute hydrochloric acid, a strong solution of ammonium chloride, and then ammonium hydroxide. A precipitate is produced. Filter, and add to the filtrate ammonium sulphide. A further precipitation takes place; the precipitate is black.

This shows that some members of this group are precipitated by NH_4OH and NH_4Cl; others only on the addition of NH_4HS.

2. Add to a solution of ferric, chromic, and aluminic chlorides $(Fe_2Cl_6, Cr_2Cl_6,$ and $Al_2Cl_6)$ ammonium chloride and hydroxide till it is just distinctly ammoniacal, and boil for a few minutes. A bulky gelatinous precipitate is obtained. Filter. Add to the clear filtrate a few drops of ammonium sulphide: no further precipitation takes place, showing that iron, chromium, and aluminium are precipitated (as hydroxides) from their saline solutions by NH_4Cl and NH_4OH alone, without the aid of NH_4HS. (Ammonium chloride has no share in the precipitation, but counteracts the solubility of the aluminium hydroxide in excess of the precipitant and prevents the partial precipitation of magnesium and some metals of Group III. if present in the solution.)

3. Dissolve some barium, strontium, calcium, and magnesium phosphates in dilute hydrochloric acid, and cautiously add ammonium hydroxide to the solution. No precipitate is produced till the free acid has been neutralised (with formation of ammonium chloride), when the phosphates are reprecipitated. Filter, and add ammonium sulphide to the filtrate. No further precipitation takes place.

This shows that the phosphates of the alkaline earthy metals are precipitated by ammonium hydroxide alone.

4. Dissolve some phosphates of Ni, Co, Mn, Zn, and Fe^{iii} in

dilute hydrochloric acid.* To one portion of the solution add
ammonium chloride and hydroxide. A precipitate is formed. The
phosphates are reprecipitated. Filter, and add ammonium sulphide;
a further precipitate is produced, showing that the phosphates of
these metals are not entirely precipitated by ammonium chloride
and hydroxide.

These two reagents precipitate :

Aluminic hydroxide and phosphate.	Nickel phosphate.
Chromic ,,	Cobalt ,,
Ferric ,,	Manganese ,,
	Zinc ,,
	Barium ,,
	Strontium ,,
	Calcium ,,
	Magnesium ,,

5. To a solution of the sulphates or chlorides (free from Fe)
of Ni, Co, Mn, and Zn add NH_4Cl in considerable excess, and then
NH_4HO in slight excess. No precipitate is obtained, because the
NH_4Cl forms double chlorides of the metals which are not affected
by NH_4HO.† To one portion of this solution add strong sul-
phuretted hydrogen water (or pass a current of sulphuretted
hydrogen gas). A copious precipitate is produced, consisting of NiS
and CoS (black), ZnS (white), and MnS (pale pink).

This shows that nickel, cobalt, manganese, and zinc salts are not
precipitated by NH_4Cl and NH_4HO, but by NH_4HS.

On exposing the other portion of the solution for some time
to the air, it is seen to turn turbid where it is in contact with the
air. Shake the solution, and the turbidity increases rapidly, show-
ing that NH_4Cl and NH_4HO produce, under favourable conditions,
a partial precipitation (owing to oxidation of the Mn compound).

6. To another portion of the solution of the phosphates of Ni, Co,
Mn, Zn, and Fe (see 4) add the chloride, hydroxide, and sulphide of
ammonium, without first separating by filtration the precipitate
produced by NH_4Cl and NH_4HO. The phosphates of Co, Ni, Mn,

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* This solution may also be prepared by adding hydrogen disodium phos-
phate to solutions of the above metals as long as a precipitate forms, and
dissolving the precipitate in a little hydrochloric acid.

† The chlorides of the metals Zn, Ni, Co, Mn also form compounds with
dry ammonia, NH_3, as represented by the zinc compound, $ZnCl_2\genfrac{}{}{0pt}{}{NH_3}{2NH_3}$. This is
the most stable of any in the group.   Its probable constitution is $Zn\genfrac{}{}{0pt}{}{NH_2.HCl}{NH_2.HCl}$.
These metals and magnesium also form compounds of the form $MgCl_2.2NH_4Cl$.
Cr and Al also form similar compounds, but they are very unstable. The dry
chlorides of Ba, Sr, Ca, and Mg also unite with dry ammonia, as $CaCl_2.2NH_3$,
as well as forming compounds with NH_4Cl. They are probably N_2H_4 or
hydrazine compounds.

The Co and Mn compounds of this class oxidise rapidly in air, Cr slower.

On adding ammonium chloride and hydroxide to chromium solutions a violet
or purple-coloured solution is often obtained. This is undoubtedly due to
the formation of a chrom-ammonium or hydrazine compound.

Zn, and Fe, which may be considered as existing in the hydrochloric acid solutions as acid or hydrogen salts, are converted into sulphides, and ammonium phosphate is left in solution.

7. To a solution of Fe_2Cl_6 add NH_4Cl and NH_4HO. A reddish-brown precipitate of ferric hydroxide, $Fe_2(HO)_6$, is produced, which on the addition of $(NH_4)_2S$ turns black.

This shows that iron is first precipitated as hydroxide, and is subsequently converted into sulphide. Some sulphur is generally precipitated in this action. Chromium and aluminium are precipitated under the same circumstances as hydroxides, as they do not form sulphides in contact with water.

It will thus be seen that the group reagents NH_4Cl and NH_4HO, for reasons stated under 4 and 5, do not thoroughly separate some of the members of Group III. from the others. The three reagents* if added together precipitate:

1. Sulphides—
$\left.\begin{array}{l} FeS \\ CoS \\ NiS \end{array}\right\}$ black. $\begin{array}{l} MnS \\ ZnS \end{array}$ pale pink or yellow.
white.

2. Hydroxides
$Al_2(HO)_6$ white. $Cr_2(HO)_6$ green.

3. Phosphates of Cr, Al, Ba, Sr, Ca, and Mg, white or nearly so.

NICKEL, Ni'' and ^{iv}.—Occurs in nature as sulphide, NiS'', in capillary pyrites, hair nickel, or millerite; as arsenide, in arsenical

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* Add ammonium hydroxide to a solution of barium, strontium, calcium (and magnesium) oxalates in dilute hydrochloric acid, as long as a white precipitate is obtained. The oxalates of the alkaline earths are reprecipitated more or less completely as soon as the hydrochloric acid which (as in the case of the corresponding phosphates) holds them in solution is completely neutralised.

The same applies to the fluorides, borates, tartrates, citrates, &c., of these earthy bases which are precipitated by NH_4HO, although in the presence of much NH_4Cl they are to a great extent held in solution.

Silicic acid and silicates, soluble in hydrochloric acid, are likewise acted upon by NH_4Cl and NH_4HO, gelatinous silica, and silicates, being precipitated.

Arsenates would also be thrown down here under the same circumstances, but in the ordinary course of procedure they are decomposed in the second group.

Notice particularly that in order to avoid complicating the qualitative course it is usually preferred to evaporate the hydrochloric acid filtrate from Group II. to complete dryness, with the addition, towards the end of the evaporation, of a little concentrated nitric acid, whenever ammonium chloride and hydroxide produce a precipitate. By these means silicic anhydride, SiO_2, is left behind insoluble in acids; the fluorides and borates are for the most part decomposed; boric and hydrofluoric acid being set free or volatilised. Oxalates are destroyed with evolution of carbon dioxide by the oxidising action of the nitric acid; and tartrates, &c., are broken up by gentle ignition into carbon and volatile gaseous products; ferrous salts are converted into ferric salts, and on extracting the ignited residue with a little concentrated hydrochloric acid the metals are obtained in solution as chlorides, together only with the phosphates of the alkaline earths, earthy and metallic bases.—See Tables.

nickel, As_2Ni, and in copper-nickel, As_2Ni_2; as antimonide, Sb_2Ni_2, in antimony-nickel, combined with sulphide, as in nickel glance or grey nickel ore, As_2Ni,NiS_2, as antimony nickel glance, Sb_2Ni,NiS_2; also in the form of minerals, which are the result of the oxidation of other nickel minerals, e.g., as nickel ochre, $Ni_3As_2O_8$, and emerald nickel, $NiCO_3,2NiO,6H_2O$, as silicate in Rewdanskite, and as nickel magnesium silicate in the important mineral garnierite, $NiMgSiO_4$.

The metal nickel is harder and tougher than iron, and exhibits a slight yellow tint on a fresh or polished surface. Its atomic weight = 57·93, specific gravity 8·9; it melts between 1150° and 1600° C. It does not oxidise appreciably at ordinary temperatures in air or in contact with water, but acts upon acids somewhat readily. It becomes decidedly magnetic, but in an inferior degree to iron.

Nickel Alloys.

Nickel, in a pure state, is employed to some extent for apparatus or ornamental articles. It is more extensively used for electro-plating iron or brass articles to prevent rusting and for æsthetic effect.

It combines with many other metals, forming most useful alloys. With brass is formed nickel silver, or German silver. This contains about 15 per cent. nickel. Cupro-nickel contains 30 to 40 per cent. nickel. The metals may be melted together in any proportion. Nickel and mild or low carbon steels—nickel steels—are somewhat numerous. Several distinct compounds with iron appear to exist (see later, " Iron ").

With some metals—for instance, aluminium—nickel combines quite violently when one or other is in a melted state.

Nickel combines with carbon in a manner similar to iron, and a characteristic compound, nickel carbonyl, is formed with carbon monoxide. This substance is formed by direct combination of carbon monoxide with the metal at about 150° C.; at a high temperature it dissociates into nickel, containing a little carbon, and CO. The compound liquefies easily, and solidifies at a low temperature. It has the composition $Ni(CO)_4$. Owing to the ease of its formation and decomposition it has become a most valuable means of extracting nickel from poor ores.

Meteoric irons contain nickel combined with phosphorus, and this combination seems to account for the Widmannstätian figures shown when polished faces of these irons are etched with an acid.

Experiments.

Metallic nickel can be obtained as wire or thin sheet.

I. Heated in an open tube, a piece of bright nickel loses its lustre, but no detachable amount of oxide is formed in a moderate time, unless some pure oxygen be sent through the tube. The oxide formed adheres closely, but may be scraped off with a knife.

II. Water has no action below 100°.

III. Heated with sulphur, the action is somewhat slow. At a moderate temperature a grey-black sulphide is formed, NiS. It is

crystalline, but not very fusible ; insoluble in water, but decomposed by acids.

IV. HCl dissolves the metal readily, with evolution of hydrogen, which smells somewhat like coal-tar, or carbon compounds. The solution is bright green ; on evaporation a yellow solid, $NiCl_2$, is left. Sulphuric acts similarly, and gives green crystals of sulphate, $NiSO_4$.

Nitric acid gives a blue-green solution. The solution on evaporation leaves yellowish crystals of NiN_2O_6—very deliquescent. On heating to redness a black oxide is left.

The oxide dissolves in acids, but not in sodium hydroxide. Freshly precipitated $Ni(HO)_2$ dissolves in ammonium hydroxide, giving a blue solution.

V. Ni exposed to moist air and ammonia gas rapidly oxidises.

VI. Melted ammonium nitrate dissolves the metal, producing a nickelamine nitrate, which on heating explodes or puffs off with much smoke.

Dry Reactions.

When nickel compounds are heated on charcoal with dry sodium carbonate in the inner blowpipe flame they are reduced to a grey metallic powder, which is feebly magnetic. Heated on a borax bead, in the outer flame, they yield an intensely coloured glass, which appears hyacinth-red to violet-brown when hot, and reddish-brown when cold. On fusing a little nitre in the bead the colour is changed to bluish or dark purple, whereby nickel compounds may be distinguished from those of iron. Heated in the reducing flame, the colour of the borax bead disappears, and it assumes a turbid grey appearance, owing to finely divided particles of metallic nickel disseminated through it. The reactions with microcosmic salt are similar, but the bead becomes almost colourless when cold.

Reactions in Solution.

Most salts are soluble. The solid salts, containing water of crystallisation, are mostly green, and their solutions are green. When heated they lose water and change to yellow, and are amorphous when they have not been melted. (Comp. also "Cobalt," p. 145.) A solution of both a nickel and a cobalt salt may be red, green, or colourless, according to the quantities present of each of the metals; when the metals are in atomic proportions the mixed solution is colourless, or practically so.

$(NH_4)_2S$ (group reagent) gives a black precipitate of nickelous sulphide, NiS, soluble in excess of the reagent, especially in the presence of free ammonia or of yellow ammonium sulphide, forming a dark brown solution—this is a good indication of nickel. The sulphide is slowly reprecipitated on boiling. The presence of ammonium chloride (or, better still, ammonium acetate) assists the precipitation. Nickelous sulphide dissolves with difficulty in dilute hydrochloric acid, but readily in nitric acid or aqua regia.

SH_2 gives no precipitate in acid solutions, and a partial precipitate only from a salt of nickel with a mineral acid, but produces

readily a precipitate from a solution of nickelous acetate, or a nickelous salt mixed with an alkali acetate, especially on heating.

NaHO, or KHO, precipitates from cold solutions an apple-green coloured hydroxide, $Ni(HO)_2$, insoluble in excess, soluble in ammonium salts to a greenish-blue fluid. Nickelous hydroxide leaves on ignition nickelous oxide. It does not absorb oxygen from the air.

NH_4OH produces a slight greenish precipitate, readily soluble in excess of hydroxide to a blue fluid. No precipitate in presence of ammonium chloride, owing to a double salt being formed.

Na_2CO_3 precipitates an apple-green basic carbonate, varying in composition.

NH_4HCO_3, same precipitate, readily soluble in excess, after washing, to a greenish-blue solution.

KCy * gives a yellowish-green precipitate of nickelous cyanide, $NiCy_2$, which dissolves readily in excess of potassium cyanide to a brownish-yellow solution, containing a double cyanide of nickel and potassium, $2KCy,NiCy_2$. On adding a dilute acid (HCl or H_2SO_4), $NiCy_2$ is reprecipitated, and the KCy is decomposed with evolution of HCy. Boiling with hydrochloric acid decomposes the nickelous cyanide also.

The solution of the double cyanide is not altered by boiling with excess of HCy, but the nickelous salt is oxidised, at the ordinary temperature, by a concentrated solution of sodium hypochlorite, ClNaO, or chlorine or bromine water, to black nickelic hydroxide, $Ni_2(HO)_6$, which is gradually precipitated; thus:

$$2NiCy_2 + ClNaO + 5OH_2 = Ni_2(HO)_6 + NaCl + 4HCy.$$
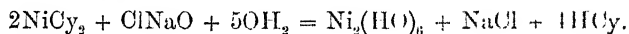
Nickelic hydroxide may also be obtained by passing chlorine through water in which nickelous hydroxide is suspended. Bromine water and then sodium hydroxide added to a nickel solution also throw down the black hydroxide. HCl decomposes the higher oxidised compound into nickelous chloride and free chlorine. A nickelic oxide, Ni_2O_3, obtained by gently heating the hydroxide, or by keeping the nitrate at a temperature of about 200° C., is a black substance, scarcely soluble in boiling acetic acid.

COBALT, Co'' and ^{iv}.—Occurs in nature as sulphide, or cobalt pyrites, Co_2S_3; as arsenide in As_2Co, tin-white cobalt or smaltine (speiss cobalt); as sulpharsenide or cobalt glance, As_2Co,CoS_4; also in the form of products of oxidation, such as cobalt vitriol, $CoSO_4,7H_2O$; as arsenate, $Co_3As_2O_8,8H_2O$, in cobalt bloom. Cobalt is generally found in small quantity in most nickel and iron ores, and in some silver ores. It resembles the metal nickel very closely; they appear almost to be right- and left-handed modifications of the same substance. Its atomic weight = 58·89. Specific gravity, 8·6. Melting-point, about 1800° C. It is slightly redder in tint than Ni, and also a little harder. When pure it behaves similarly to Ni as regards air

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* Potassium cyanide is seldom pure enough to give this reaction cleanly. The salt should be recrystallised from alcohol when required for this test.

and water and acids.   It also becomes slightly magnetic.   Cobalt is not quite so abundant nor is it so much used as nickel.   Cobalt does not form a compound with CO.

Cobalt Alloys.

These are not numerous, although the metal seems to act very like nickel towards copper, aluminium, and other metals.

Both cobalt and nickel form a definite crystalline compound with tin, of the composition CoSn and NiSn respectively.   These compounds are quite insoluble in dilute mineral acids.

Experiments.

These results are to be compared with those from nickel.

Metallic cobalt can be obtained in thin electro-deposited plates, or in small pieces from fusion.

I. Heated in air, the metal becomes covered with a film of oxide, but slowly.

II. Water has no action at 100°.

III. Sulphur combines slowly, forming black CoS.

IV. Acids act with about the same ease as on nickel.   With HCl the solution is pink, and becomes blue on evaporating ; finally a blue mass of $CoCl_2$ is left, which is very soluble in water.

H_2SO_4 acts similarly when heated and not too dilute.   On evaporating nearly to dryness, red crystals of $CoSO_4$ are formed.

HNO_3 acts more rapidly.   The solution is pink when dilute, and blue when concentrated, and on complete evaporation a blue very deliquescent mass is left.   Further heating gives black oxide, Co_3O_4. This is soluble in acids, and gives the same salts as from the metal. The nitrate is $CoN_2O_6 + Aq.$

V. Alkalies have no action either on metal or oxide.

VI. Ammonium nitrate, melted, dissolves the metal more rapidly than it does nickel.   A rosy-coloured cobaltamine nitrate and nitrite is produced, which explodes when heated.

Dry Reactions.

Cobalt is usually detected with comparative facility.   Cobalt minerals containing sulphur or arsenic are roasted on charcoal, or in a glass tube, when sulphurous and arsenious anhydrides are evolved. The residue is then introduced into a borax bead, and heated in the outer flame, when a fine blue-coloured bead is obtained.   This colour remains the same both in the outer and inner, or reducing, flame. In cases where much Mn, Fe, Cu, or Ni are mixed with Co, the blue appears distinctly only after the bead has been heated for some time in the reducing flame.   Microcosmic salt gives a similar blue bead. Heated on charcoal with sodium carbonate in the reducing flame, cobalt separates as a grey metallic powder, which is attracted by the magnet.   Potassium cyanide is more effective than the carbonate as a reducing agent.

Reactions in Solution.

Cobalt salts are mostly red or pink when crystalline and hydrated. The solutions are also red. When dehydrated they become blue. The solutions also, when concentrated and warm, are blue, and turn pink on cooling or diluting. Strong solutions of cobalt salts seem, as a matter of fact, to dehydrate in the presence of water. The addition of a strong acid, as HCl or HNO_3, to a cobalt solution will change the colour from pink to blue.

$(NH_4)_2S$ (group reagent) gives a black precipitate of cobaltous sulphide, CoS, insoluble in excess of the reagent, and very difficultly soluble in dilute hydrochloric or sulphuric acid, but readily soluble in aqua regia upon the application of heat. Hence a black residue left, on treating the ammonium sulphide precipitate of Group III. with dilute hydrochloric acid, indicates probably the presence of cobaltous or nickelous sulphide.

SH_2 gives no precipitate from an acid solution, but precipitates cobaltous sulphide partially from a neutral solution, and wholly from a solution of cobaltous acetate, or from a solution of a cobaltous salt containing a mineral acid on the addition of an alkali acetate.

KHO or NaHO gives a precipitate of a blue basic salt which turns olive-green on exposure to air, owing to the absorption of oxygen. On heating in very dilute solutions a rose-red cobaltous hydroxide, $Co(HO)_2$, is obtained, which, however, often contains a small amount of the dark brown oxide. Ammonium carbonate dissolves the precipitate (after filtration and washing) to an intensely violet-red fluid. This contains the salt of a cobaltamine.

By suspending cobaltous hydroxide in water, and passing a current of chlorine into it, black cobaltic hydroxide is precipitated, cobaltous chloride remaining in solution ; thus :

$$3Co(HO)_2 + Cl_2 = Co_2(HO)_6 + CoCl_2.$$
<div align="center">Cobaltic
hydrate.</div>
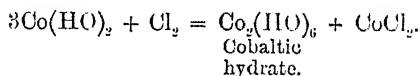
In the presence of an alkali (NaHO) the whole of the cobaltous hydroxide is converted into cobaltic hydroxide. Br or I act as well as Cl.

NH_4HO produces in neutral solutions a slight precipitate of a basic salt, which dissolves readily in excess. The solution is reddish-brown. Ammonium chloride prevents the precipitation altogether. The solution, however, absorbs oxygen from the air, and becomes red on standing, a roseo-cobaltamine being formed.

Na_2CO_3 precipitates a peach-coloured basic carbonate.

$(NH_4H)CO_3$, same precipitate ; readily soluble in excess to a red solution.

KCy gives with all neutral cobaltous salts a brownish-white precipitate of cobaltous cyanide, $CoCy_2$, soluble in excess, reprecipitated by dilute hydrochloric or sulphuric acid.

N.B.—In case the cobaltous solution should contain free acid, so that it liberate hydrocyanic acid by the action of the latter upon the
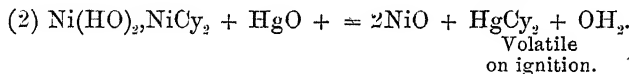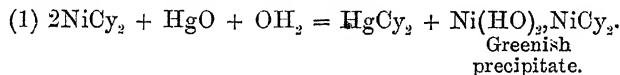
excess of KCy, also if the solution containing the double cyanide, $2KCy,CoCy_2$, be heated in the air for some time, dilute hydrochloric or sulphuric acid will no longer produce a precipitate, the whole of the cobaltous cyanide having been converted into cobaltic cyanide, Co_2Cy_6, which remains combined with $6KCy$ to form a well-defined and stable salt, potassium cobalticyanide, $K_6Co_2Cy_{12}$, hydrogen being evolved ; thus :

$$2CoCy_2 + 2HCy = Co_2Cy_6 + H_2.$$
$$6KCy + Co_2Cy_6 = K_6Co_2Cy_{12}.$$
<div align="center">Potassium
cobalticyanide.</div>
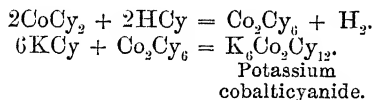
This salt is not acted upon by a cold solution of sodium hypochlorite. It corresponds closely to potassium ferricyanide. From it free cobalticyanic acid may be obtained. A series of salts of this acid is known (see later).
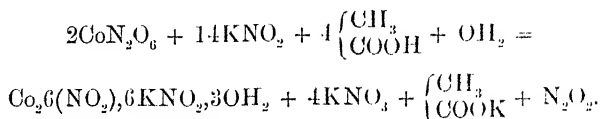
Separation of Nickel from Cobalt.—The hydrocyanic acid reaction affords a good method of separating nickel from cobalt. To a slightly acid solution of the two salts add cautiously, drop by drop, a solution of potassium cyanide as long as a precipitate forms, and till the precipitate is just redissolved and the yellowish-brown turbid liquid has become clear. Boil for some time in a well-ventilated place, to avoid inhaling fumes of HCN which escape, allow to cool, and add a moderate quantity of bromine water, chlorine water—or a hypochlorite such as bleaching-powder solution will do as well—and then NaOH. $Ni_2(HO)_6$ is precipitated on gently warming, and cobalt remains in solution as $K_6Co_2Cy_{12}$. Separate by filtration. Test the residue in a borax bead for nickel, and evaporate a part of the solution to dryness and test for cobalt by means of a borax bead.

Instead of separating nickel as $Ni_2(HO)_6$ by means of hypochlorite or Br water and NaOH, the solution, after digesting with excess of HCy or KCy, may also be precipitated whilst hot with freshly precipitated and washed mercuric oxide. On digesting for a short time at a gentle heat the whole of the nickel is precipitated, partly as $Ni(HO)_2$, partly as $NiCy_2$, the mercury combining with the liberated cyanogen. Filter off the greenish or yellowish-grey precipitate, wash, and ignite. Pure NiO is left ; thus :

(1) $2NiCy_2 + HgO + OH_2 = HgCy_2 + Ni(HO)_2,NiCy_2.$
<div align="center">Greenish
precipitate.</div>

(2) $Ni(HO)_2,NiCy_2 + HgO + = 2NiO + HgCy_2 + OH_2.$
<div align="center">Volatile
on ignition.</div>

The cobalt remains in the solution as $K_6Co_2Cy_{12}$. Nearly neutralise with dilute nitric acid, and add a neutral solution of mercurous nitrate, $Hg_2(NO_3)_2$. A white precipitate of mercurous cobalticyanide, $Hg_3Co_2Cy_{12}$, forms, which contains the whole of the cobalt. Filter, wash, and ignite under a hood with free access of

Another method of separation consists in adding a concentrated solution of pure KNO_2 (potassium nitrite) in considerable excess to a concentrated neutral solution of the two metals, then acetic acid until acid to test paper. On keeping the solution in a moderately warm place the nickel salt remains in solution, and the whole of the cobalt separates in the form of a crystalline precipitate of a fine yellow colour (from a dilute solution only after long standing), the formation of which is expressed by the equation:

$$2CoN_2O_6 + 14KNO_2 + 4\begin{cases}CH_3\\COOH\end{cases}H + OH_2 =$$

$$Co_2 6(NO_2), 6KNO_2, 3OH_2 + 4KNO_3 + \begin{cases}CH_3\\COOK\end{cases} + N_2O_2.$$

Yellow precipitate.

The precipitate is perceptibly soluble in cold, and more readily still in hot water; it is decomposed by hot nitric or hydrochloric acid, or by potassium hydroxide; insoluble in alcohol and in the presence of potassium acetate; and it can therefore be washed by a solution of potassium acetate, and finally with alcohol. This reaction separates nickel from cobalt very effectually.[*]

From the filtrate the nickel is best precipitated as the apple-green basic carbonate by a fixed alkali carbonate, or as the peroxide by addition of bromine water and an alkali.

The presence of Ba, Sr, or Ca salts interferes with the reaction, triple nitrites of Co, Ni, and one of the other metals being formed, nickel forming similar compounds with Ba, Sr, or Ca to those which cobalt forms with the alkali metals.

On igniting $Ni(NO_3)_2$, a dirty greyish powder of NiO is left. $Co(NO_3)_2$, heated gently at about $200°$ in an air-bath, leaves black cobaltous dicobaltic tetroxide, Co_3O_4, which is not soluble in boiling dilute acetic acid. On treating this oxide with hydrochloric acid chlorine gas is evolved, according to the equation:

$$Co_3O_4 + 8HCl = 3CoCl_2 + Cl_2 + 4OH_2.$$
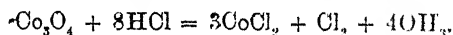
Both nickel and cobalt are capable of forming compounds in which the metals exist in a triad condition, viz:

Ni_2O_3,	Co_2O_3,	and	Co_2S_3.
Nickelic oxide.	Cobaltic oxide.		Cobaltic sulphide.
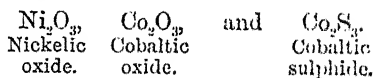
Ni_2O_3 is, however, mostly obtained in the presence of water by the action of oxidising agents, and cannot exist at a high temperature.

Co_3O_4, on the other hand, is obtained in the dry way, or on gentle ignition of cobaltous salts containing volatile acids, and gives up a portion of its oxygen only on strong ignition.

The same tendency to form a compound in which cobalt exists as a tetrad element is observed on exposing the freshly precipitated

[*] This reaction can evidently not be used for hurried work.

hydroxide to the air, or on passing chlorine or adding bromine or iodine to cobaltous solutions.

Little use has been made of these reactions for analysis purposes beyond the conversion of $CoCy_2$ into Co_6Cy_6, in the presence of potassium cyanide, or of CoO into Co_2O_3 in the potassium nitrite reaction.

MANGANESE, Mn'', ^{iv}, and ^{vi}.—Atomic weight, 54·8; specific gravity, 8·0. It melts at about 1900° C. Occurs in nature in various states of oxidation, forming oxides, of which the mineral pyrolusite, MnO_2, is the most important. It is found in small quantities in many iron ores, and is a frequent constituent of silicates, the MnO replacing the isomorphous bases, FeO, ZnO, MgO, CaO, without altering the crystalline structure of the minerals. It exists both in the dyad and tetrad condition in manganous and manganic oxides. The anhydrous oxides known, besides pyrolusite, are braunite, Mn_2O_3, hausmannite, Mn_3O_4; the hydrated oxides are manganite, Mn_2O_3,H_2O, psilomelane, wad, varvicite, copper-mangan, &c. Manganese is found in combination with sulphur in manganese blende, MnS; with carbonic acid in diallogite, $MnCO_3$; with silica in red manganese or mangan kiesel (rhodonite), $MnSiO_3$; and in tephroite, Mn_2SiO_4; with phosphoric acid as triplite, $Mn_3Fe_2P_2O_9$.

Manganese is not used exactly in the pure metallic state, but is largely employed as an alloy with iron, as spiegeleisen, manganese steel, and in some bronzes, &c. Spiegeleisen, or ferromanganese, is an essential " reagent " in the manufacture of steel by the " open hearth " and the " Bessemer " processes. In both processes an oxide of iron is produced and dissolved by the " steel." Ferromanganese is added at the final stage in the process. The manganese removes the oxygen compound, forming a fusible slag, and the carbon of the ferromanganese " carburises " the steel. Manganese combines also with and removes sulphur from melted iron or steel. Manganese can be obtained in a compact state by reduction of the oxide with aluminium powder, in which form it is sometimes used for preparing alloys, with copper and other metals. It imparts considerable hardness to alloys. Manganese bronze, a compound of manganese and copper, is a very valuable alloy. Manganese is not magnetic. The powdery metal obtained by reduction of the oxide by carbon oxidises very rapidly in air and water, and dissolves in most acids, but the compact metal is not very easily acted upon.

Experiments.

I. HCl dissolves MnO_2 (and other oxides); chlorine is evolved on heating. On evaporating, a pale pink mass of $MnCl_2$ is left.

II. Alkalies are without action in solution, but when melted form a green mass of alkali manganate.

III. With the metal. Metallic Mn powder heated in air oxidises, frequently glowing and forming a red or brown powder.

IV. HCl dissolves the metal slowly, giving off H, which contains

some hydrocarbon. Diluted nitric and sulphuric also dissolve it, but the concentrated acids have little action.

V. The finely powdered metal oxidises very rapidly when dropped into melted nitre.

Dry Reactions.

The presence of manganese is readily detected in minerals which contain no other oxides capable of colouring fluxes, as they dissolve when heated in the outer flame, in the borax bead, or in a bead of microcosmic salt, to a clear violet-red colour, which becomes of a fine amethyst colour on cooling. The bead becomes colourless when heated in the reducing flame. If other metallic oxides are present it is preferable to mix a small trace of the finely powdered manganese compound with two or three times its weight of sodium carbonate (a little nitre should also be added), and to fuse on platinum foil (a small platinum spoon or the lid of a platinum crucible) in the oxidising flame, or over the tip of the Bunsen, when a bluish-green mass is left after cooling, consisting of sodium manganate, Na_2MnO_4. The mass at the same time loses its transparency. This forms the most characteristic and delicate reaction for manganese. Manganous and manganic oxides are converted by this treatment into a higher oxide, perhaps Mn_2O_7.

Reactions in Solution.

The sulphate and chloride are, soluble and common. Solid hydrated manganous salts are pinkish in colour.

All the higher oxides of manganese, when heated with hydrochloric acid, evolve chlorine, and are converted into manganous chloride. The chlorine so evolved is sometimes taken as a measure of the amount of MnO_2 present in a manganese ore.

Dilute solutions of pure manganous salts are colourless.

$(NH_4)_2S$ (group reagent) gives a flesh-coloured precipitate of manganous sulphide, MnS, readily soluble in dilute acids, even acetic acid. Hence the presence of free acetic acid prevents the precipitation of manganese by SH_2 (method of distinguishing Co and Ni from Mn). The manganese may be separated by repeating once or twice the precipitation of cobalt and nickel in the presence of acetic acid.

SH_2 does not precipitate a neutral solution of a manganous salt ; the acetate is acted upon but very slowly and imperfectly, and not at all when free acetic acid is present.

KHO or NaHO gives a white precipitate of manganous hydroxide, $Mn(HO)_2$, insoluble in excess. The precipitate speedily absorbs oxygen from the air, and turns dark brown with formation of Mn_2O_3,H_2O, which then no longer dissolves completely in ammonium chloride.

NH_4HO precipitates a white hydrated oxide from neutral solutions ; insoluble in excess, or in ammonium carbonate. It rapidly absorbs oxygen. No precipitate is produced in solutions containing ammonium chloride. On exposing an ammoniacal solution of the soluble double chloride, $2NH_4Cl,MnCl_2$, to the action of the air, the whole of the manganese is gradually precipitated as dark-brown

manganic hydroxide, Mn_2O_3,H_2O. This reaction is characteristic for manganese compounds, and distinguishes it from zinc, nickel, &c. In this change the ammonia conveys oxygen to the manganous salt in a manner similar to the action it has upon cobaltous salts, or upon metallic copper, in the presence of oxygen or air. That is, a small quantity of manganamide is produced, which rapidly becomes oxidised and passes the oxygen to the manganese itself.

Owing to this tendency of manganous salts to become oxidised and precipitated in the presence of free ammonia, it is not possible to completely separate manganous from ferric salts by means of ammonium chloride and hydroxide. The reddish-brown ferric hydroxide, which is precipitated, invariably carries down more or less Mn_2O_3,H_2O; and small quantities of manganese cannot, therefore, be separated from iron by precipitation with these reagents. The separation succeeds best if the excess of ammonia be immediately boiled off.

Na_2CO_3 or K_2CO_3 precipitates white manganese carbonate, $MnCO_3$, insoluble in excess of the reagent, but pretty readily soluble in ammonium chloride. This precipitate also absorbs oxygen from the air, and turns to a dirty brownish-white colour, owing to the formation of manganic oxide or hydroxide. On ignition with free access of air the white carbonate turns first black, and changes subsequently to brown trimanganic tetroxide, Mn_3O_4. All manganese oxides are finally obtained upon ignition in the air in the form of Mn_3O_4. Both Mn_2O_3 and Mn_3O_4 are compounds of MnO with MnO_2.

KCy gives a whitish precipitate of manganous cyanide, $MnCy_2$, soluble in excess to a brown solution, which is not precipitated by ammonium sulphide. Manganous compounds, soluble or not, are very readily oxidised on contact with water and chlorine, bromine, or iodine, or a hypochlorite to MnO_2H_2O :

$$MnCl_2 + ClNaO + 2OH_2 = MnO_2,H_2O + NaCl + 2HCl.$$
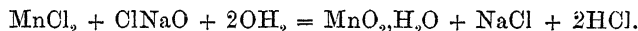
By fusion with dry sodium carbonate, alone or together with nitre, the manganous or manganic compounds are converted into an alkali manganate, in which the metal manganese acts the part of a hexad element. Only the alkali manganates dissolve in water, giving green solutions.

Manganates are readily decomposed in aqueous solutions. On gently heating a solution of potassium manganate, with free access of air, the green colour changes to purple-red, owing to the formation of potassium permanganate, $K_2Mn_2O_8$, and separation of hydrated dioxide and alkali hydroxide, thus:

$$3K_2MnO_4 + 3OH_2 = K_2Mn_2O_8 + MnO_2,H_2O + 4KHO.$$
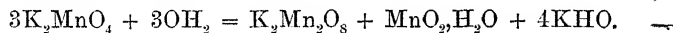
The change is accelerated by adding a few drops of a dilute mineral acid, e.g., nitric, hydrochloric, or sulphuric acid, which combines with the liberated alkali and manganese oxide.

The manganese seems to act here the part of a pseudo-octad element; and it may readily be inferred that the different oxygen atoms perform different functions in such a highly oxygenised com-

pound, and that the manganese will part with some more readily than with others.

Manganic dioxide, as well as other peroxides, also the alkali manganates and permanganates, act as powerful oxidisers, differing merely in the extent of their oxidising action.

Manganic dioxide gives off oxygen on warming with concentrated sulphuric acid, and forms normal manganous sulphate :

$$2MnO_2 + 2H_2SO_4 = O_2 + 2MnSO_4 + 2OH_2.$$
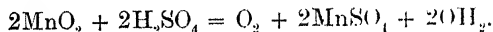
Sulphuric acid added to sodium, or other manganate, gives off oxygen, and forms sulphates, thus:

$$Na_2MnO_4 + 2H_2SO_4 = O_2 + MnSO_4 + Na_2SO_4 + 2OH_2.$$
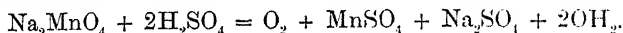
Sulphuric acid added to a solution of potassium permanganate liberates five atoms of oxygen, and leaves manganous and potassium sulphates in the solution when something is present capable of taking up the oxygen.

$$2K_2Mn_2O_8 + 6H_2SO_4 = 5O_2 + 4MnSO_4 + 2K_2SO_4 + 6OH_2.$$
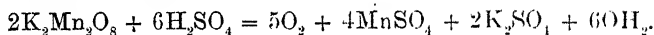
Note.—This equation is true if the permanganate be added to hot moderately strong sulphuric acid. When added, in powder, to cold concentrated H_2SO_4, the first reaction is

$$K_2Mn_2O_8 + H_2SO_4 = K_2SO_4 + H_2O + Mn_2O_7.$$
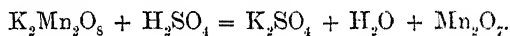
This substance Mn_2O_7 collects in oily drops on the sulphuric acid. They have a beetle-green lustre, and give off a pink vapour. Contact with almost any kind of combustible substance, as sulphur, phosphorus, carbon compounds, especially solid benzenoid hydrocarbons, will cause a violent explosion. *Very little* of this substance must be made at once, as a slight elevation of temperature also causes violent decomposition. The substance distils over along with steam, and condenses, yielding free permanganic acid.

Hydrochloric acid also reacts with the higher oxides of manganese, with evolution of chlorine and formation of metallic chlorides and water. Potassium permanganate and hydrochloric acid form the most convenient chlorine "generator" on a small scale. The peroxides of manganese, especially the black oxide, constitute the principal substances, used together with hydrochloric acid, or sodium chloride and oil of vitriol, for evolving chlorine both in the laboratory and on a manufacturing scale.

No other mineral oxidising agent is capable of yielding from one molecular group of elements five atoms of oxygen; and there are but few substances which resist the oxidising action of potassium permanganate. Hydrogen, freshly ignited charcoal, phosphorus, iodine, sulphur, sulphuretted hydrogen, carbon disulphide, hydrocarbons and organic bodies generally, are oxidised more or less rapidly. The rate and products differ according as the solution is acid or alkaline.

Most of the common metals are oxidised in contact with a permanganate and an acid. This action is not so general when the solution

is alkaline. Iron is not in the least affected in an alkaline solution. Many lower oxides, chlorides, &c., are converted into higher oxides, &c., especially in the presence of a free acid (hydrochloric or sulphuric). Thus arsenious is converted into arsenic acid, sulphurous into sulphuric, nitrous into nitric, phosphorous into phosphoric acid. Oxalic acid is oxidised into carbon dioxide and water. Lower or -ous chlorides, sulphates, &c., are converted into the higher or -ic salts ; e.g., ferrous, stannous, antimonious, cuprous, and mercurous chlorides are oxidised or " chlorinised," in the presence of free hydrochloric acid, into ferric, stannic, antimonic, cupric, and mercuric chlorides. The manganese and potassium of the permanganate are left in solution as chlorides. Ferrous, cuprous, and other sulphates are converted in the presence of free sulphuric or hydrochloric acid into ferric, cupric, &c., sulphates.

The reaction in all these cases is indicated by a change of colour. On adding, for instance, the purple-coloured permanganate solution to a solution of sulphurous acid the colour is instantly destroyed as long as any sulphurous acid is left. Permanganate is a quantitative measure for sulphurous acid, and in like manner for other lower oxides, chlorides, organic substances, &c.

Sulphurous acid requires one atom of oxygen in order to be converted into sulphuric acid ; as one molecule of potassium permanganate can part with five atoms of oxygen, one molecule of the oxidising agent oxidises five molecules of the reducing agent—i.e., 316 parts by weight of potassium permanganate are the measure for $5 \times 64 = 320$ parts by weight of SO_2.

Two molecules of ferrous sulphate in the presence of sulphuric acid combine with one atom of oxygen to form one molecule of ferric sulphate, thus : $2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O$. Hence one molecule of potassium permanganate oxidises ten molecules of $FeSO_4$, ten molecules of FeO, or ten atoms of Fe ; so that 316 parts by weight of $K_2Mn_2O_8$ are a measure for—

$$10 \times 152 \text{ parts by weight of } FeSO_4$$
$$\text{or } 10 \times 72 \quad \text{,,} \qquad FeO$$
$$\text{or } 10 \times 56 \quad \text{,,} \qquad Fe.$$

ZINC, Zn''.—Occurs in nature chiefly as sulphide or zinc blende, black jack, ZnS ; as carbonate, or calamine, $ZnCO_3$; and as silicate, or zinc glance, electric calamine, Zn_2SiO_4,OH_2, willemite, Zn_2SiO_4 ; also as oxide in red zinc ore, ZnO. The red colour is due to oxides of iron and manganese.

The metal being volatile at a high temperature is extracted from its oxide by distillation with carbon. It is of a decided blue tint ; highly crystalline, and somewhat brittle when cold, but becomes malleable when heated to about 120° C. Its atomic weight = 64·90 ; specific gravity, 7·15 ; melting-point, 360° C. ; boiling-point, about 1040° C. It oxidises superficially in air, and decomposes water slowly at its boiling-point (100° C.), and steam rapidly at a red heat. It dissolves in most acids, mineral or organic, displacing two equivalents of hydrogen. It is also dissolved by the alkali hydroxides

when they are fused or in aqueous solution. Ammonium hydroxide dissolves it in presence of air, and the metal decomposes also gaseous ammonia when heated in it. Ammonium nitrate in a melted state attacks the metal very violently. Its water solution also dissolves the metal without evolution of gas. Most ammonia salts are decomposed more or less rapidly by zinc.

Zinc oxide is neither fusible nor volatile at temperatures below that of burning hydrogen or the electric arc. It is used in some incandescence lamp mantles.

Zinc is more electro-positive than most other common metals, and as it dissolves both in acids and alkalies can "reduce" most of the per- or -ic salts of these metals to a lower state of combination, or even to the metallic state. It reduces solutions of salts of Fe, Cr, Co, Mn, Ni, Mo, Ti to their lowest stage of combination, and Cu, Pb, Sn, Sb, As, Ag, Cd, Bi, Au, and Pt to the metallic state.

For this reason it is largely used as the positive element in several forms of galvanic coil.

In a state of powder, known as zinc dust—really a mixture of the metal and hydroxide—it is used to "reduce" some organic compounds, or deprive them of oxygen or halogens and add hydrogen.

With some organic radicals, as methyl (CH_3), ethyl (C_2H_5), &c., it forms a series of compounds, mostly volatile, which are self-igniting in contact with air. This is especially the case with zinc methyl, $Zn(CH_3)_2$ and zinc ethyl, $Zn(C_2H_5)_2$.

Zinc Alloys.

The metal unites with most other metals, but few of the compounds or alloys possess the physical properties generally required for practical purposes. Its most useful combination is with copper, constituting brass. Muntz metal contains zinc, copper, iron; and many "bronzes" contain small quantities of the metal. "Galvanised" iron is a *surface* alloy of zinc on iron, prepared either by dipping the clean iron article into melted zinc or by electro deposition. The idea in its employment is that the zinc will oxidise first and preserve the iron. It does this also because the zinc oxide "sticks" fast on the surface of the metal, and thus protects it from rapid oxidation like a coating of varnish, whilst iron oxide peels off almost as rapidly as formed.

Many triple alloys, such as zinc-aluminium-tin, have found specific uses.

Zinc does not unite with lead to the extent of more than 1 per cent.

Experiments.

I. Zinc heated in air melts, with formation of a film of oxide, which soon wrinkles. The metal when hot enough vapourises and burns with a blue flame; a crust of oxide forms. This oxide, ZnO, is yellow whilst hot and white on cooling. It does not melt or vapourise.

II. Water has little visible action below 100°.

III. Just melted with sulphur, very little action takes place, or only a superficial one.   Strongly heated, to vapourising, in a hard tube, a somewhat energetic combination takes place.   It is best to heat up quickly over a blowpipe.

IV. HCl and H_2SO_4 (dilute) dissolve the metal rapidly, evolving hydrogen.   The sulphuric acid solution on evaporation easily gives white crystals of $ZnSO_4,7H_2O$.   The HCl solution on evaporation yields a syrup, $ZnCl_2$, which at a red heat gives off whitish vapours. On cooling it sets into a white or sometimes glassy mass.   It is *extremely* deliquescent and soluble.

Nitric acid acts very rapidly; red fumes are evolved.   The solution contains ZnN_2O_6, which is left on careful evaporation as a similar substance to the chloride.

Alkalies dissolve the metal on heating, liberating hydrogen and forming white compounds, as $ZnOK_2O$.   If Fe or Pt be present the action is more vigorous.

The oxide dissolves very easily both in acids and alkalies, including ammonium hydroxide.

Dry Reactions.

The most characteristic blowpipe reaction for zinc consists in the white incrustation of zinc oxide which its compounds yield when heated on charcoal in the reducing flame with sodium carbonate. The zinc compound is reduced to the metallic state, and the metal, being volatile, burns, on passing through the outer flame, with a bluish-green flame, and is converted into oxide, which covers the charcoal with an incrustation, yellow when hot, white when cold, and which assumes a fine green colour when treated with a solution of cobaltous nitrate and once more strongly heated in the outer flame.   The incrustation is not driven away in the oxidising flame —zinc oxide being non-volatile.

Zinc compounds give with borax or microcosmic salt in both flames a bead, which is yellowish whilst hot and white on cooling; opaque if much zinc salt be present.   This applies, however, only to pure zinc compounds, and the detection of zinc by the blowpipe in poor ores containing other readily oxidisable metals (such as Pb, Cd, As, Sb, which likewise give incrustations) is a matter of great uncertainty.   The borax bead test is quite unreliable for zinc.

Zinc sulphide (zinc blende), when roasted in a tube of hard glass, loses part of its sulphur in the form of sulphur dioxide, and forms some zinc sulphate, $ZnSO_4$ (white vitriol), which may be extracted with water.

Both calamine and blende on thorough roasting leave zinc oxide.

Reactions in Solution.

Most zinc salts are soluble in water, the chloride and nitrate extremely so.   They are only coloured when the acid is coloured, or a chromogen.

$(NH_4)_2S$ (group reagent) gives a white precipitate of zinc sulphide, ZnS, insoluble in excess.   From dilute solutions the precipitate

separates only after some time, but more speedily in the presence of ammonium chloride. It is readily decomposed by dilute hydrochloric and sulphuric acids, with the evolution of sulphuretted hydrogen; also by nitric acid, but is insoluble in acetic acid.

SH_2 precipitates zinc imperfectly from neutral solutions of zinc salts with mineral acids; but from an acetate or a solution of a zinc salt mixed with an alkali acetate the whole of the metal is precipitated by sulphuretted hydrogen as zinc sulphide, even in the presence of much acetic acid. (Method of separation of Zn from Mn.)

KHO or NaHO precipitates the white $Zn(HO)_2$, readily soluble in excess, also in ammonium hydroxide; reprecipitated almost entirely on largely diluting with water and boiling; soluble also in ammonium chloride. Sulphuretted hydrogen precipitates the whole of the zinc from these solutions. In the presence of the hydroxides of manganese, nickel, and cobalt, KHO or NaHO does not readily dissolve out the whole of the zinc hydroxide.

Na_2CO_3 or K_2CO_3 produces a white precipitate of basic carbonate, consisting of two molecules of zinc carbonate and three molecules of hydroxide, according to the equation:

$$5ZnSO_4 + 5Na_2CO_3 + 3OH_2 = 2ZnCO_3, 3Zn(OH)_2 + 5Na_2SO_4 + 3CO_2.$$
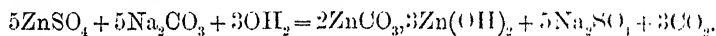
A large excess of ammonium salts prevents this.

On ignition this carbonate leaves ZnO, zinc oxide, also known in commerce under the name of zinc white.

Ammonium carbonate produces the same precipitate, soluble, however, in excess.

KCy gives a white precipitate of zinc cyanide, $ZnCy_2$, soluble in excess, not reprecipitated by $(NH_4)_2S$, but completely precipitated by sodium or potassium sulphide, as ZnS. (Method for the separation of Zn from Ni.)

Metallic zinc precipitates less electro-positive metals from their solutions, viz., As, Sb, Sn, Cd, Cu, Pb, Ag, Bi, Hg, and on dissolving impure metallic zinc in dilute acids (hydrochloric or sulphuric) these metals do not dissolve as long as any zinc remains undissolved. Hence zinc protects other metals, such as copper, iron (galvanised iron), &c., from the oxidising action of air, water, and acids.

Zinc, when placed in contact with platinum, iron, &c., dissolves in cold alkaline solutions. (See Experiments, ante.)

Zinc vapour decomposes CO_2 at a high temperature, and forms ZnO and CO. ZnO, however, yields its oxygen to carbon. (Method of extracting metallic zinc from its ores. It is much more likely that in the extraction of zinc from ZnO the large excess of CO present in the retort may really do all the reduction, in addition to carrying the zinc vapour forward to the outlet.)

IRON, Fe″, [iv], and [vi].—Occurs very abundantly in nature, mostly in a state of combination with oxygen and sulphur. It is also found as "meteoric iron", and in some very old rocks also in the metallic state,

but very finely divided.   There are a great number of iron minerals known, but it will suffice if some of those iron ores suitable for the extraction of iron are mentioned.   The most important are :

1st. Ores containing ferrous oxide : spathic or sparry iron ores, $FeCO_3$, containing varying quantities of $MnCO_3$, $MgCO_3$, and $CaCO_3$; black band or carbonaceous iron ore, containing from 20 to 25 per cent. of bituminous matter; clay ironstone is, as its name indicates, associated with clayey matter.   It is from these two ores that the greater part of the iron manufactured in this country is derived. They occur in immediate proximity to the coal measures and lime-stone beds—the fuel and flux employed in their reduction to the metallic state.   Some of these contain phosphates in some quantity.

2nd. Ore containing ferrous and ferric oxides—viz., magnetic iron ore, Fe_3O_4.

3rd. Ores containing ferric oxide only—viz., red hæmatite (micaceous iron, oligist, specular iron, or iron glance), Fe_2O_3.   This oxide forms different compounds with water which, according to the amount they contain, have received different names—viz., turgite, $2Fe_2O_3,OH_2$; needle iron ore, brown iron ore, or pyrrhosiderite, Fe_2O_3,OH_2 ; limonite or compact brown iron ore, brown hæmatite, $2Fe_2O_3,3OH_2$; varieties : oolitic iron ore (pea ore); yellow iron ore or xanthosiderite, $Fe_2O_3.2OH_3$.

A few other iron ores deserve attention.   They are not used for the extraction of iron, but are valuable as a cheap source of sulphur —viz., iron pyrites, martial pyrites or mundic, FeS_2, found abun-dantly in nature ; copper pyrites, Fe_2S_3, Cu_2S, and magnetic pyrites, $5FeS$, Fe_2S_3 or Fe_7S_8.

Besides these ores, iron is found in nature in combination with arsenic and sulphur, in mispickel, $FeAs_2,FeS_2$; with chromium as chrome iron ore, FeO,Cr_2O_3; with silica as chloropal, $Fe_2(SiO_3)_3,3H_2O$, and many other silicates ; as sulphate, in green copperas or green vitriol, $FeSO_4,7OH_2$; as phosphate in vivianite,* $Fe_3P_2O_8,8OH_2$ (fer-rous phosphate) ; as arsenate, in scorodite, $Fe_2As_2O_8$, and others.

All the oxides of iron part readily with their oxygen when heated with carbon, carbon monoxide, or hydrogen.

Pure metallic iron is silver-white on a fresh surface, which is very permanent in dry air, but rapidly changes, by oxidation, in moist air containing carbon dioxide or nitrous acid or sulphur compounds. Its atomic weight is 55·88.   Specific gravity, 7·86.   Melting-point of iron is given by Pictet as 1600° C., by Carnelly as 1804° C.—both doubtful.   Varieties of iron, as cast iron, steel, &c., melt at a much lower temperature—from 1050° to 1400° C.   All varieties, wrought iron, cast irons, steel, and some alloys are eminently magnetic.

Iron unites with a considerable number of other elements, metallic or non-metallic, and its physical properties are as a rule very con-siderably modified even by the presence of small amounts of these combining substances.   Carbon, silicon, phosphorus, oxygen, and other non-metals are in this respect particularly effective.

* Contains also ferric phosphate, $Fe_2P_2O_8.8OH_2$, to which the blue colour of the mineral is due.

With metals proper but few combinations or alloys have come into common use.

One, with zinc (galvanised iron), has been mentioned. A similar one is formed with tin. They are both surface alloys, and the physical properties of the iron are therefore little affected. Iron can be melted up with silver, platinum (and other metals of the platinum group), nickel, and cobalt, several compounds resulting in each case, the properties of which would not exclude them from being useful, although, for a number of reasons, only one of these - iron-nickel—has taken a prominent place.

With lead or mercury iron refuses to combine under any conditions, and with copper only to a very small extent, the alloy having no sufficiently striking properties to recommend it.

With the non-metals C, Si, Ti, Vd, Cr, Mn, Mo, and W combinations, or alloys, are formed, many of which have become useful for special purposes. These alloys are generally termed steels, although that term should be restricted to the carbon compounds. They are very different in their physical properties from iron proper, although the quantities of these "affecting" elements is in each case very small—from less than 1 per cent. to 3 or 4 per cent. only. Stated generally, the properties exhibited by the iron compounds of the above-named non-metals are hardness and tenacity (or toughness) of different degrees and kinds.

The non-metals oxygen, sulphur, phosphorus, and arsenic, on the other hand, induce more or less undesirable properties, as brittleness, which detract from the malleability or workableness of the iron or steel, and in some cases cause an irregular physical structure and consequent lowering of tensile strength.

Metals are essentially crystalline solids, but in many the crystalline structure is to a great extent suppressed by the heat or mechanical treatment they have undergone. Iron may be obtained in distinct crystals by electrolysis of a solution of ferrous ammonium sulphate, but although irons and steels show under the microscopic distinct "structure" it is scarcely correct to call them crystals. Iron presents some allotropic modifications.

Carbon easily combines with iron. The product from the blast furnace may contain 3 per cent. or more, in addition to other substances, refined or cast iron about 2 per cent., and steels from 1·6 per cent. down to ·10. In steels the carbon is undoubtedly in the form of a carbide of iron of the composition CFe_3, which can unite with iron at certain temperatures to form definite complexes or solid solutions. Steel with about ·9 per cent. of carbon is considered by some authorities to represent a definite substance, perhaps CFe_{24}, to which all the peculiar properties of steel are due. Steels with more than 1 per cent. carbon are spoken of as "high" or "hard," and with less than ·5 as "mild," "low," or "soft" steels.

When steel is melted and allowed to solidify and then cool it exhibits several checks or pauses in the rate or curve of cooling. The temperatures at which these occur vary a little, depending on the content of carbon, but roughly they are about 870° C. (A_3), 760° C.

(A$_2$), and 670° C. (A$_1$).   These are " critical " temperatures, at or around which molecular changes take place.   Heat-energy is given out at these points.

The diagram, copied from Osmond, shows the transformation periods of iron and, as the microscopic examination of steels teaches,
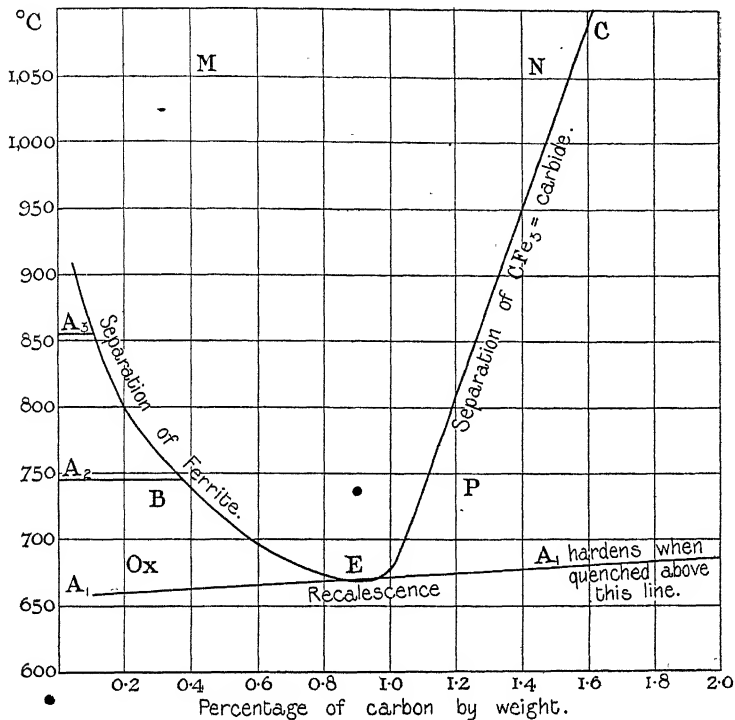

FIG. 57.

the conditions of separation of iron, or ferrite, or of the carbide, CFe$_3$, or cementite (see Fig. 57).

The horizontal portion corresponds to a separation of the two constituents in alternate layers as " pearlite."   The diagram shows that steel above BEC is a homogeneous solid solution of the carbide.   During slow cooling either iron (ferrite) or carbide (cementite) is deposited as it becomes saturated with either one, until a definite composition is reached.   Allotropic changes in the iron at different temperatures act similarly to solidification of a solution of a salt.

Steels cooled slowly from a certain high temperature may be mixtures of ferrite and pearlite (see Figs. 59, 60, 61, 62), pure pearlite, or pearlite and cementite, according as the carbon is inferior, nearly equal, or superior to the proportion in the "eutectic."   Many impurities

or other metals affect considerably the composition of the carbon-iron eutectic.

If steel be rapidly cooled or chilled, it becomes more or less hardened. The changes that take place in slow cooling are prevented. The carbon (or carbide) retains the character it had at a high temperature. It is said to be in the "state of hardening carbon." It is just possible that the iron whilst acting as a solvent for the carbon is to some extent in an allotropic form.

To quote from Osmond, "if steel be rapidly chilled from some temperature above the curve B E C (in Fig. 57), ferrite, pearlite, and cementite disappear. Two cases are possible, according as the proportion of carbon is inferior or superior to that of the eutectic. Taking as an example a steel with about ·4 per cent. carbon, and chilling from 1050° C. (M of Fig. 57), an apparently homogeneous structure composed of needle-like figures (Fig. 60) results.

"It has been called martinsite. Usually the martinsitic needles become smaller and less evident as the eutectic is approached, and hardness at the same time rises to its maximum. A steel with more than 1 per cent. carbon, chilled at 1050° (N of Fig. 57), separates into two structures. If the chilling take place only after cooling to below B E C, but still above A₁ (say 680°), the structures which have formed during the gradual cooling from 1050° to this temperature will be found.

"Thus steel of ·3 per cent. C, chilled at 720° C. (O point, Fig. 57), will exhibit ferrite along with martinsite; steel with 1·24 per cent. C, chilled at 735° (point P, Fig. 57), will show cementite along with martinsite.

"Heating to temperatures not exceeding A₁ (670°, about) and chilling has no effect on steels, the structures appearing to be rigid."

Experiments.

I. On heating in air, a clean and bright surface of iron or steel changes through many colours, becoming, finally, black, rough, and sometimes blistered. Heated to full redness, black scales form, which easily detach and become reddish when exposed to damp or when rubbed. = Fe_3O_4. Steel is a little slower than iron in showing these changes.

II. Ordinary iron or steel placed in ordinary water rusts more or less rapidly. Water containing CO_2 or H_2O_2 acts most rapidly. In the absence of free CO_2 or any free acid and H_2O_2, or when the water is made alkaline, no rusting takes place. Steam passed over heated iron or steel oxidises the metal, rapidly producing a black or red coating of oxide, depending on the temperature.

III. Iron or steel filings heated with sulphur; combination takes place readily, FeS being produced.

IV. Many acids dissolve iron. The hydrogen given off has a strong odour of hydrocarbons (of the C_nH_{2n} and C_nH_{2n}—two series). Pure iron gives a clear, very light green solution, from which crystals of $FeCl_2$ can be obtained. Cast irons and steels leave a greater or less amount of black residue (carbon and graphite).

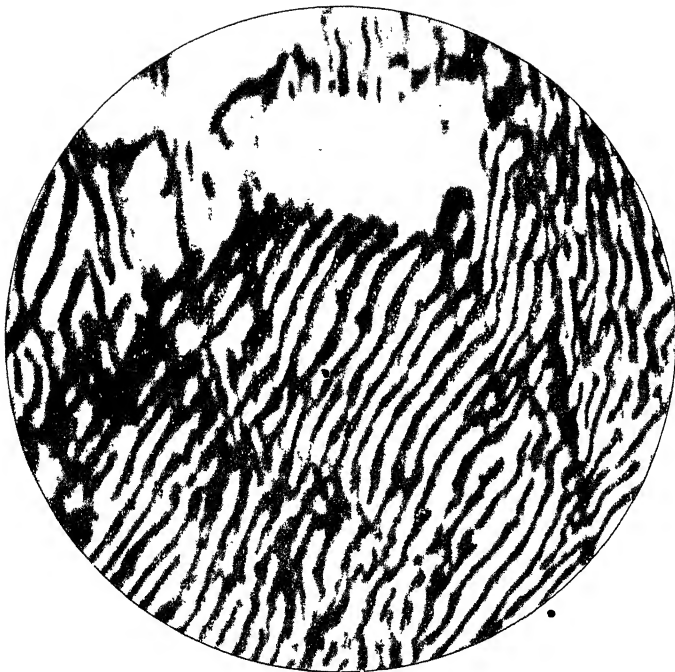H_2SO_4, dilute, behaves similarly, producing $FeSO_4$.

FIG. 58.—Steel-pearlite. (× 3000.)
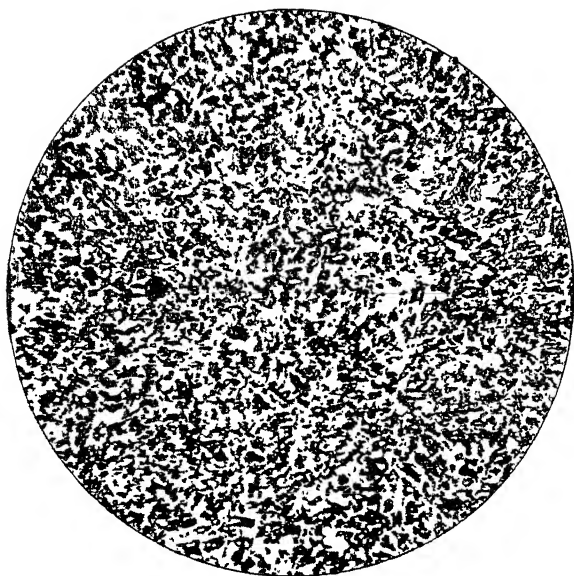
FIG. 59.—A mild steel (·36 per cent. carbon), heated for
two hours at 780° C. and cooled moderately slowly
in muffle.   (× 100.)

FIG. 60.—The same steel heated to 1050° for two
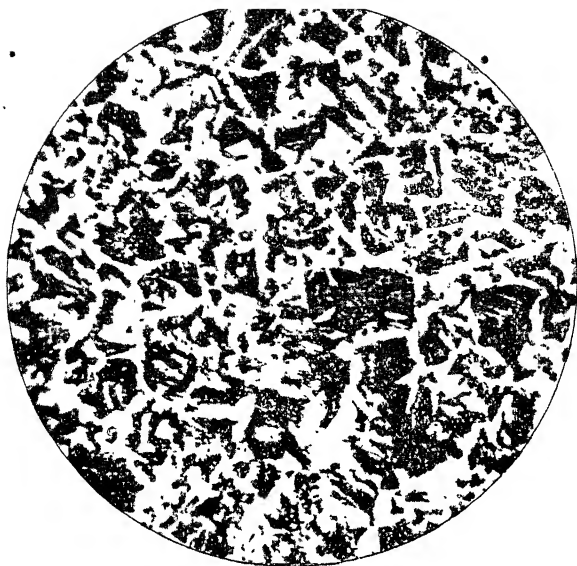hours and cooled in air.   (× 100.)

FIG. 61.—Steel of ·36 per cent. C., heated two hours at
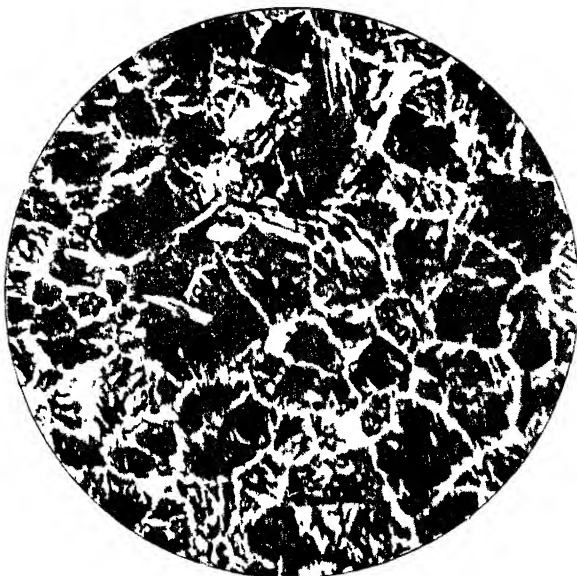870° C. and cooled in muffle. (× 100)
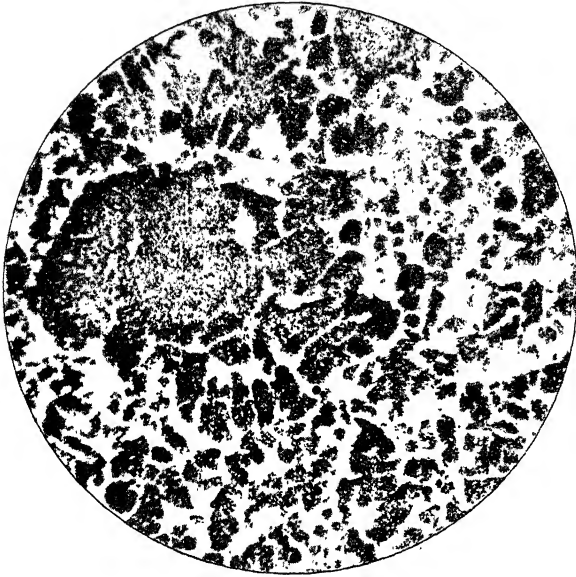

FIG. 62.—The same steel heated for two hours at
870° C. and cooled in air. (× 100.)

FIG. 63.—A nickel steel (Ni 3·5 per cent., C. ·3 per cent.)
heated to 780° and cooled slowly. (× 100).

Nitric, moderately dilute, acts violently; red gases are evolved, and a red or green solution of ferric or ferrous nitrate formed, depending on amount and strength of the acid used. With steels the solution is generally *brown*, owing to the combined carbon being acted upon and dissolved.

Concentrated sulphuric and nitric acids have no action on iron. On diluting the acids an action may start, but not always with nitric acid—the surface of the metal may require scratching or touching with a more positive metal, as zinc.

V. Alkalies, including ammonia, have no action either on metallic iron or its oxides. Bright steel or iron is not affected by any alkaline oxidising agents.

The red oxide produced in I. or II. ($= Fe_2O_4$) dissolves in acids, giving red ferric salts.

Dry Reactions.

On heating the different iron compounds on charcoal before the blowpipe, they leave a black magnetic residue. When heated in the outer flame on a borax bead iron compounds impart a dark red colour to the borax whilst hot, becoming light yellow when cold. In the reducing flame they give an olive-green to bottle-green bead.

The reactions with microcosmic salts are similar but less distinct The presence of Co, Cu, Ni, Cr, conceals the colour of the iron bead. Ferric sulphides and arsenides must be roasted previous to being introduced into the borax bead. When heated with Na_2CO_3 on charcoal, in the reducing flame, metallic iron is obtained as a black magnetic powder.

Reactions in Solution.

Iron forms two series of salts—viz., ferrous and ferric salts. The metal dissolves readily in dilute acids, such as HCl, H_2SO_4, forming ferrous salts, $FeCl_2$, $FeSO_4$, with evolution of hydrogen. Cold, very dilute nitric acid dissolves finely divided iron (iron filings) without evolving hydrogen gas, the nitric acid being decomposed, so as to form ferrous nitrate and ammonium nitrate; the reaction may be expressed thus : $4Fe + 10HNO_3 = 4Fe(NO_3)_2 + NH_4NO_3 + 3OH_2$.

Iron exists in all these salts in the dyad condition, but exhibits a marked tendency to pass into a higher stage. Exposed to the air, solutions of $FeCl_2$ and $FeSO_4$ absorb oxygen, and are gradually converted into ferric salts. The same change is produced by the action of various oxidising agents, such as Cl, Br, I, ClNaO, $KClO_3$, and in the presence of HCl by HNO_3, $AgNO_3$, $AuCl_3$, $K_2Mn_2O_8$, K_2CrO_4, and others. Ferrous compounds are, therefore, powerful *reducing* agents, and are frequently employed as such.

A. *Ferrous compounds.**—Either the sulphate or chloride may be

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* Ferrous sulphate forms a number of so-called double sulphates with the alkali metal sulphates and ammonium sulphate. $FeSO_4(NH_4)_2SO_4,6H_2O$ is much used in volumetric work, as it is easily obtained very pure, and contains almost exactly one-seventh of its weight of iron.

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used for reactions. Ferrous salts are mostly green when hydrated and white when anhydrous.

$(NH_4)_2S$ (group reagent) gives a black precipitate of ferrous sulphide, FeS, almost insoluble in alkalies and alkali sulphides, easily decomposed and dissolved by dilute hydrochloric acid, with evolution of sulphuretted hydrogen. The moist precipitate absorbs oxygen from the air, and is rapidly converted into ferrous sulphate, and lastly into yellow basic ferric sulphate, with evolution of much heat. (This oxidation constitutes a frequent cause of the spontaneous inflammation of pyritical coal (which contains sulphides of iron) in mines and on board vessels.)

SH_2 does not precipitate neutral or acid solutions of ferrous salts; ferrous acetate even is only partially precipitated.

Alkali hydroxides and ammonia, also CaH_2O_2 and BaH_2O_2, precipitate from ferrous salts (free from ferric salts) white ferrous hydroxide, $Fe(HO)_2$, which turns rapidly to a dirty green colour, and ultimately becomes reddish-brown, owing to absorption of oxygen from the atmosphere. Ammonium salts partially prevent the precipitation by the fixed alkalies, and ammonium hydroxide gives but a slight precipitate in a ferrous solution, containing a considerable amount of ammonium chloride. The presence of non-volatile organic acids, of sugar, &c., also prevents the precipitation more or less.

Soluble carbonates precipitate white ferrous carbonate, $FeCO_3$, which becomes rapidly oxidised when exposed to air.

$K_4Fe(CN)_6$ (potassium ferrocyanide) produces by the replacement of K_2 by Fe a bluish-white precipitate of potassium ferrous ferrocyanide, $K_2Fe''Fe(CN)_6$, thus:

$$FeSO_4 + K_4Fe(CN)_6 = K_2''Fe(CN)_6 + K_2SO_4,$$
<div align="center">Bluish-white
precipitate.*</div>
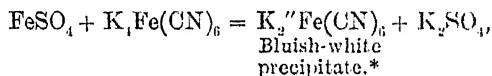
insoluble in dilute hydrochloric acid. The light blue precipitate is rapidly converted into a dark blue precipitate, or Prussian blue, either by exposure to the air, or more speedily by an oxidising agent (in solution), thus:

$$4K_2Fe''Fe(CN)_6 + 2Cl_2 = Fe_4(Fe(CN)_6)_3 + 4KCl + K_4Fe(CN)_6.$$
<div align="center">Prussian
blue.*</div>
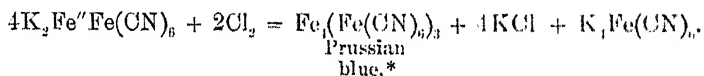
$K_6Fe_2(CN)_{12}$ † (potassium ferricyanide) produces a dark blue precipitate of ferrous ferricyanide, $Fe_3Fe_2(CN)_{12}$ (Turnbull's blue), insoluble in hydrochloric acid, thus:

$$3FeSO_4 + K_6Fe_2Cy_{12} = Fe''_3Fe'''_2Cy_{12} + 3K_2SO_4.$$
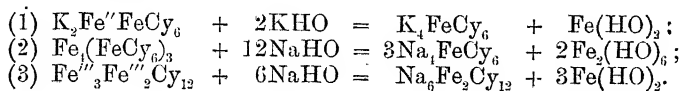<div align="center">Turnbull's blue.*</div>
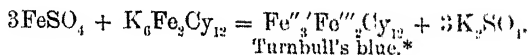
NaHO or KHO decomposes both precipitates with formation of

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* These precipitates cannot form, therefore, in an alkaline solution.
† This may be written K_3FeCy_6.

soluble alkali ferro- and ferri-cyanides, and separation of ferrous and ferric hydroxides, thus :

(1) $K_2Fe''FeCy_6$ + $2KHO$ = K_4FeCy_6 + $Fe(HO)_2$:
(2) $Fe_4(FeCy_6)_3$ + $12NaHO$ = $3Na_4FeCy_6$ + $2Fe_2(HO)_6$;
(3) $Fe'''_3Fe'''_2Cy_{12}$ + $6NaHO$ = $Na_6Fe_2Cy_{12}$ + $3Fe(HO)_2$.

N.B.—Cy is the abbreviation for (CN), the cyanogen radical. The molecule of cyanogen is C_2N_2.

NH_4SCN (ammonium sulphocyanate) gives no coloration, if the ferrous solution contain no ferric salt, but the test is very delicate, and most generally sufficient ferric salt is present to give a faint red coloration.

B. *Ferric compounds.*—A solution of ferric chloride, Fe_2Cl_6,[*] may be used.

$(NH_4)_2S$ (group reagent) produces a black precipitate of ferrous sulphide, FeS, *mixed with sulphur*, thus :

$$Fe_2Cl_6 + 3(NH_4)_2S = 2FeS + S + 6NH_4Cl.$$
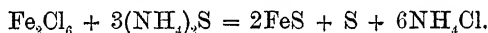
Dilute solutions of iron give only a greenish coloration.

On dissolving the black precipitate in dilute hydrochloric acid, sulphuretted hydrogen is evolved, and white insoluble sulphur is left. (Distinction between ferrous and ferric salts.) Ferric sulphide cannot be formed in the wet way; native sulphides exist, however— viz., FeS_2 and Fe_2S_3—which are insoluble in dilute hydrochloric acid, but dissolve with evolution of SH_2 when in contact with metallic zinc.

SH_2 does not precipitate Fe_2Cl_6; its hydrogen acts as a reducing agent upon the ferric salt, converting it into $2FeCl_2$ and $2HCl$, *white sulphur* being precipitated, which renders the solution of the ferrous salt milky.

Alkali hydroxides and ammonia, also calcium or barium hydroxides, precipitate the reddish brown $Fe_2O_3,2OH_2$, insoluble in excess and in ammonium salts (excepting the carbonate). Non-volatile organic bodies (*e.g.*, tartaric or citric acid, sugar, &c.) prevent its precipitation by ammonium hydroxide, but not by ammonium sulphide. The precipitate retains with great tenacity small portions of the fixed alkalies.

Na_2CO_3 and K_2CO_3 produce the same precipitate with evolution of carbon dioxide.

Hydrogen disodium phosphate produces a yellowish-white, floccu-lent, gelatinous precipitate of ferric phosphate, $Fe_2P_2O_8 + 4OH_2$. The precipitation is complete only in the presence of an alkali acetate, thus :

$$Fe_2Cl_6 + 2Na_2HPO_4 + 2CH_3CO_2Na = Fe_2P_2O_8 + 6NaCl + 2CH_3CO_2H.$$

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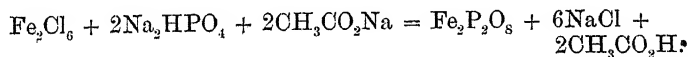
[*] This formula, Fe_2Cl_6, may be considered as " convenient," and is retained' for that reason only. $FeCl_3$ is, no doubt, the real constitutional formula, as indicated by the vapour density of the anhydrous salt.

On the addition of the first few drops of hydrogen disodium phosphate, and as long as the ferric salt is largely in excess, the precipitate may disappear again, especially on gently warming, since it is somewhat soluble in ferric acetate. When the precipitation is nearly complete, the ferric phosphate separates more speedily, especially on stirring and gently heating, and allowing to subside after each addition of the phosphate solution. The precipitated ferric phosphate should be filtered hot, and washed by decantation with hot water. It is soluble in dilute mineral acids —hence the addition of an alkali acetate ; insoluble in acetic acid (like the corresponding chromic * and aluminic phosphates).

Phosphates of the metals Ba, Sr, Ca, Mg, which are readily soluble in acetic acid, may thus be separated by filtration from the phosphates of Fe^{iv}, Al^{iv} (and Cr^{iv}). Owing to this property of ferric phosphate, it is also possible to decompose alkaline earthy phosphates in a solution containing an excess of sodium acetate, by adding, drop by drop, a neutral solution of ferric chloride, according to the equation :

$$2BaHPO_4 + 2CH_3CO_2Na + Fe_2Cl_6 = Fe_2P_2O_8 + 2BaCl_2 + 2NaCl + 2CH_3CO_2H.$$
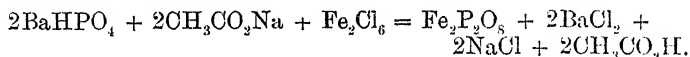
The ferric chloride must be added as long as a yellowish white precipitate comes down, and till the supernatant liquid becomes just red, from the formation of ferric acetate.

Ferric phosphate dissolves in excess of hydrogen disodium phosphate, in the presence of ammonium hydroxide or carbonate, to a brownish red solution. It is somewhat soluble in ferric, but not in ferrous, acetate. Ammonium hydroxide reduces it to a basic phosphate. Potassium or sodium hydroxide removes nearly the whole of the acid. Fusion with caustic fixed alkalies, or with fusion mixture, or boiling with ammonium sulphide, decomposes ferric phosphate completely, leaving the iron as oxide or sulphide, from which the soluble alkali phosphate can be separated readily by filtration.

Citric or tartaric acid prevents the precipitation of ferric phosphate from solutions.

K_4FeCy_6 gives a fine blue precipitate, $Fe_4(FeCy_6)_3$, known as Prussian blue, thus : $2Fe_2Cl_6 + 3K_4FeCy_6 = Fe_4(FeCy_6)_3 + 12KCl$. Insoluble in hydrochloric acid; decomposed by KHO or NaHO; soluble in oxalic acid and also in excess of K_4FeCy_6, to a blue solution.

$K_6Fe_2Cy_{12}$ produces no precipitate, but the yellow colour of the ferric solution changes to reddish brown. (Distinction between ferrous and ferric salts.)

NH_4SCN (ammonium sulphocyanate) gives a dark red or blood-red colour, even in the case of very dilute solutions, which is not destroyed by hydrochloric acid. The sensitiveness of the reaction is heightened by shaking a hydrochloric acid solution, to which the

* Chromic phosphate, especially when freshly precipitated, is dissolved, although with some difficulty, in acetic acid, especially on heating.

sulphocyanate has been added, with ether. The blood-red ferric sulphocyanate, $Fe_2(SCy)_6$, being soluble in ether, becomes thus concentrated into a small bulk of liquid. Very small amounts of iron can be detected by this means. The colour of the liquid is readily destroyed by a solution of mercuric chloride (also by tartaric or phosphoric acid). (Distinction of Fe″ from Fe^{iv}.)

Excess of sodium acetate, added to a solution of ferric salt, produces a deep red coloured liquid, owing to the formation of ferric acetate. On diluting and boiling, the whole of the iron is precipitated as basic ferric acetate in the form of brownish yellow flakes, which should be filtered hot and as quickly as possible when the fluid has become clear. (Method of separating Fe^{iv} from Mn″.)

Ammonium succinate or benzoate precipitates ferric, but not ferrous, salts, as ferric succinate or benzoate.* The ferric solution should be perfectly neutral. Salts of Mn, Co, Ni, Zn are not precipitated. (Method of separation of Fe^{iv} from Fe″, Mn, Ni, Co, Zn.)

Freshly precipitated and well washed barium or calcium carbonate, suspended in water, precipitates ferric (not ferrous) chloride, as ferric hydroxide, $Fe_2(HO)_6$, mixed with basic salt, with evolution of carbonic dioxide. The reagent is added to the neutral ferric salt in the cold, and well shaken up with it till the reddish brown precipitate acquires a whitish appearance, from excess of the earthy carbonate.

Barium carbonate separates in like manner the higher or -ic chlorides of this group from the lower or -ous chlorides. In order to separate ferric from ferrous compounds, or ferric, chromic, and aluminic compounds from ferrous, zinc, manganous, cobaltous, and nickelous salts, it is necessary that these metals should all be obtained in the form of chlorides. On the addition of barium carbonate, the respective hydroxides, mixed with basic salts, are precipitated from the ferric, chromic and aluminic chlorides, whilst ferrous chloride and the chlorides of Zn, Mn, Ni, and Co are not affected. Air has to be excluded as carefully as possible, in order to prevent the oxidation of the ferrous, manganous, and cobaltous hydrates during the operation. The reaction should be performed in a small flask, filled nearly to the neck with the liquid, and kept well corked, after the evolution of the carbon dioxide has ceased. The addition of ammonium chloride, previous to the precipitation with barium carbonate, almost entirely prevents *any* cobaltous or nickelous hydrates from falling out with the barium carbonate precipitate. (Method for separating Fe^{iv} (also Al and Cr) from Fe″, Zn″, Mn″, Ni″, and Co″.)

The precipitate is filtered off, and dissolved in hydrochloric acid, the barium removed by means of dilute sulphuric acid, and the Fe, Cr, and Al precipitated by ammonium hydroxide.

Tannic as well as gallic acid (tincture of nut-galls) produces from neutral ferric salts a bluish black precipitate (ink), readily soluble with decomposition in acids.

* The formulæ of these compounds will be explained under the respective acids.

Ferric salts can act as oxidising agents in some cases. • Thus sulphurous acid, H_2SO_3, is converted into H_2SO_4; KI gives off iodine; $Sn''Cl_2$ is converted into $Sn^{iv}Cl_4$; $Na_2S_2O_3$ (sodium thiosulphate) is oxidised to $HNaSO_4$. It is generally necessary for an acid to be present. Iron, zinc, or magnesium readily reduce ferric to ferrous salts. Magnesium reduces iron to the metallic state from ferrous salts.

C. Ferric anhydride, FeO_3, or ferric acid, H_2FeO_4, containing hexad iron, has never been obtained in an uncombined state. The alkali salts only are known, and are obtained by fusing ferric oxide with nitre or with potassium peroxide. Ferrates are decomposed far more readily than manganates.

CHROMIUM, Cr'', ^{iv}, and ^{vi}. Atomic weight $= 52·45$; specific gravity, $6·50$. Its melting-point is not known with certainty, but is higher than that of platinum.—This metal is used as an alloy with iron. It is quite easily obtained in a compact state by the reaction between aluminium powder and Cr_2O_3. The temperature produced is very high, and the product is melted chromium. It is very hard and crystalline. Chrome steel may be made by heating to a very high temperature chrome iron ore and cast iron with excess of carbon. As obtained by reduction of the chloride, Cr_2Cl_6, with sodium or magnesium, metallic chromium is crystalline, and about the colour of iron, but is not so dense or hard as that obtained by the aluminium process. It scarcely oxidises in air, and dissolves but slowly in acids. Fused with an alkali nitrate or hydroxide, the metal oxidises, forming a chromate. This element is not very widely distributed. It occurs in nature chiefly as chrome iron ore, Cr_2O_3FeO, and crocoisite, $PbCrO_4$. Chromic oxide constitutes the colouring-matter in ruby, green serpentine, &c. Many of its compounds are employed as colours.

Experiments on Chrome Steel.

I. Acids dissolve it very slowly. The more Cr the slower the action. Strong nitric is the best solvent. On evaporating to dryness in a small dish, adding a little (solid) KNO_3, and fusing, a mass consisting of Fe_2O_3 and K_2CrO_4 is left. Water dissolves the K_2CrO_4, giving a yellow solution.

II. Ferro-chrome or other alloy will also give K_2CrO_4, on direct fusion with KNO_3; better with Na_2O_2 and KNO_3.

[Most compounds are made from chrome iron ore, $FeCrO_4$, by fusion with alkalies and decomposition of the alkali chromate formed.]

III. Chromium oxide, Cr_2O_3, heated alone, does not change. Acids dissolve it, forming green salts. The sulphate, Cr_23SO_4, is a purple-green crystalline substance.

The oxide scarcely changes on heating with sulphur.

Ammonia has no action on it, but strong $NaHO$ solution dissolves the precipitated oxide. After intense ignition the oxide is almost unaffected by acids. All alkalies and alkali carbonates, also CaO, give

chromates on fusion with the oxide ; they are yellow, crystalline, and soluble.

Dry Reactions.

Chromium compounds are readily recognised by the very characteristic green colour which the oxide imparts to borax and microcosmic salt, especially in the reducing flame.   Finely powdered chrome iron ore, or other very insoluble and difficultly decomposable chromium compounds, fused for a few minutes in a platinum spoon or crucible with four times its weight of hydrogen potassium sulphate, and then again with the addition of an equal bulk of nitre and potassium carbonate, yields a yellow mass of potassium chromate, K_2CrO_4, which is soluble in water to a yellow solution.   If manganese were present, the solution would be green, owing to the formation of potassium manganate.   This latter can be readily removed by adding a few drops of alcohol to the solution, heating, and filtering off the manganic hydroxide.   The chromate remains unchanged in the alkaline solution.

Reactions in Solution.

Chromic salts can be prepared from the yellow K_2CrO_4, or the red potassium dichromate, $K_2Cr_2O_7$, by heating with strong hydrochloric acid and adding alcohol, when the yellow solution changes to a deep green solution of Cr_2Cl_6.*

Chromium is capable of forming at least three series of compounds—

Chromous compounds.	Chromic compounds.	Chromates.
$Cr''Cl_2$.	$'Cr'''_2Cl_6$.	K_2CrO_4.
$Cr''O$.	$'Cr'''_2O_3$.	$PbCrO_4$.
$Cr''(HO)_2$.	$'Cr'''_2(HO)_6$.	&c.,
&c.	&c.	

of which the two latter are best known.

A. *Chromic Compounds.*—The sulphate or double sulphate with K or Na (CrAlum), chloride, nitrate, or acetate, are soluble and easily obtained salts.

$(NH_4)_2S$ (group reagent) precipitates bluish green chromic hydroxide, $Cr_2(HO)_6$, insoluble in excess.

NH_4OH precipitates the same, somewhat soluble in excess, the fluid acquiring a pink tint.   This is probably due to a chrome-ammonium compound produced by oxidation.   On boiling for a few minutes the precipitation is generally complete.

KHO or NaHO, same precipitate, readily soluble in excess of the cold reagent to a green solution; reprecipitated by long-continued boiling, or on adding NH_4Cl, whereby the fixed alkali is removed as KCl or NaCl, with liberation of ammonia.

Na_2CO_3 or K_2CO_3 gives a greenish precipitate of basic carbonate (varying in composition), somewhat soluble in excess.
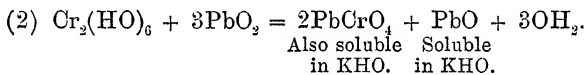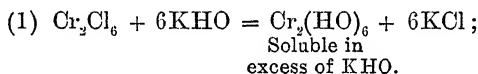
* This is most probably $CrCl_3$.

HNa_2PO_4 (hydrogen disodium phosphate) precipitates green chromic phosphate, $Cr_2P_2O_8$, soluble in mineral acids, difficultly soluble in acetic acid.

Barium carbonate precipitates a basic carbonate. The precipitation takes place cold, but is completed only after long digestion—two or three days.

In the presence of citric, tartaric, and oxalic acid, and also of sugar, the precipitation of chromic salts by means of ammonium, sodium, or barium carbonate is more or less incomplete.
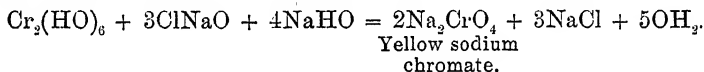
Chromic compounds may be recognised also by converting the chromic oxide into chromic acid. This may be accomplished—

1st. By boiling a solution of Cr_2Cl_6 with PbO_2 and KHO or NaHO. The reaction which takes place, and which is indicated by a change of colour (from green to yellow) may be expressed thus:

$$(1)\ Cr_2Cl_6 + 6KHO = Cr_2(HO)_6 + 6KCl;$$
<div style="text-align:center">Soluble in
excess of KHO.</div>

$$(2)\ Cr_2(HO)_6 + 3PbO_2 = 2PbCrO_4 + PbO + 3OH_2.$$
<div style="text-align:center">Also soluble   Soluble
in KHO.   in KHO.</div>

On acidulating the solution with acetic acid a precipitate of lead chromate, $PbCrO_4$, is obtained.

2nd. By boiling a solution of Cr_2Cl_6 with NaHO and sodium hypochlorite, ClNaO, or bleaching powder, $CaOCl_2$, thus:

$$Cr_2(HO)_6 + 3ClNaO + 4NaHO = 2Na_2CrO_4 + 3NaCl + 5OH_2.$$
<div style="text-align:center">Yellow sodium
chromate.</div>

3rd. By fusion with alkali carbonates and nitre on platinum foil.

B. Chromium trioxide, CrO_3, combines with water to form chromic acid, H_2CrO_4. This forms with monad metals two classes of salts, the normal or yellow chromates, viz., e.g., K_2CrO_4, and the dichromates, e.g., $K_2Cr_2O_7$, isomorphous with the corresponding sulphates and disulphates. A solution of the neutral potassium chromate is changed to an orange-red (acid) dichromate solution on the addition of an acid, thus:

$$2K_2CrO_4 + 2HCl = K_2Cr_2O_7 + 2KCl + OH_2.$$
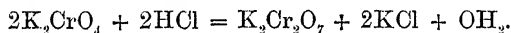
Conversely, the dichromate is transformed into a chromate on the addition of an alkali, thus:

$$2K_2Cr_2O_7 + 2KHO = 2K_2CrO_4 + OH_2.$$
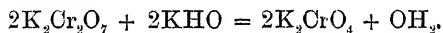
Trichromates, and even higher stages of oxidation, are also known, and may be obtained by treating an alkali, or other chromate, with nitric acid, which removes some of the positive metal. They are less soluble than the normal alkali salts, more intensely coloured, and generally crystallise well.

Chromic anhydride may be prepared by slowly adding to a cold saturated solution of the red potassium dichromate $1\frac{1}{2}$ times its bulk of concentrated sulphuric acid. As the liquid cools down, CrO_3 crystallises out in brilliant crimson-red prisms. The mother-liquor is poured off, and the crystals placed to drain upon a porous tile or slab of unglazed porcelain (biscuit ware), or in a funnel which has been lightly plugged with asbestos. They must be protected from moist air, as the substance is extremely hygroscopic.

Chromic anhydride is a very powerful oxidising agent. Four molecules of CrO_3 yield upon ignition chromic oxide and three molecules of oxygen, according to the equation $4CrO_3 = 2Cr_2O_3 + 3O_2$.

### Reactions of CrO_3 based upon its Oxidising Action.

A solution of potassium dichromate, $K_2Cr_2O_7$, will show these. SH_2, in the presence of free hydrochloric acid, reduces the orange-red solution to a green liquid, sulphur being precipitated, thus:

$$K_2Cr_2O_7 + 8HCl + 3SH_2 = Cr_2Cl_6 + 2KCl + 7OH_2 + S_3.$$
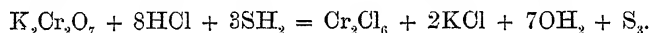
A little H_2SO_4 is generally formed.

$(NH_4)_2S$, added in excess to a solution of an alkali chromate or dichromate, precipitates dirty green hydrated chromic chromate. On boiling, the whole of the chromium separates as green chromium hydroxide thus:

$$K_2Cr_2O_7 + 3(NH_4)_2S + 7OH_2 = Cr_2(HO)_6 + S_3 + 2KHO + 6NH_4OH.$$
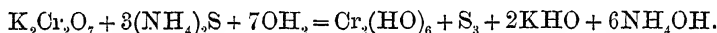
The action is much more complex than here given, some of the S becoming oxidised to SO_3, which combines with the ammonia, forming $(NH_4)_2SO_4$. The amount of S oxidised is generally about a third of that represented as liberated in the above equation. On heating, NH_3 escapes, sulphide and sulphate of potassium being left in solution.

SO_2 or H_2SO_3, in the presence of a little free acid, reduces potassium dichromate to chromic sulphate, thus:

$$K_2Cr_2O_7 + 3H_2SO_3 + H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 4OH_2.$$
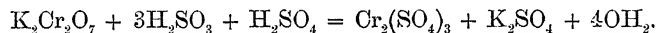
Chromic sulphate and potassium sulphate constitute potassium chrom-alum, $K_2Cr_2(SO_4)_4$.

Oxalic acid, in the presence of free acid (dilute sulphuric), produces the same reduction, carbon dioxide being evolved. Six molecules of CO_2, or three of oxalic acid, are the measure for one molecule of potassium dichromate.

$$K_2Cr_2O_7 + 3H_2C_2O_4 + 4H_2SO_4 = K_2Cr_2(SO_4)_4 + 6CO_2 + 7OH_2.$$
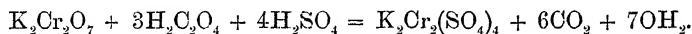
Hot concentrated sulphuric acid decomposes the dichromate, with evolution of oxygen and formation of potassium chrom-alum, thus:

$$2K_2Cr_2O_7 + 8H_2SO_4 = 2K_2Cr_2(SO_4)_4 + 8H_2O + 5O_2.$$
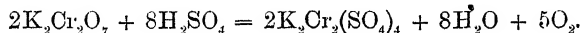
HCl (concentrated) evolves chlorine, and the hydrogen com
with the three available atoms of oxygen in the dichromate thu

$$K_2Cr_2O_7 + 14HCl = Cr_2Cl_6 + 2KCl + 7OH_2 + 3Cl_2.$$
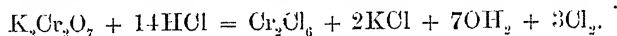
H_3AsO_3, arsenious acid (in a hydrochloric acid solution), is
verted into H_3AsO_4, thus :

$$K_2Cr_2O_7 + 3H_3AsO_3 + 8HCl = Cr_2Cl_6 + 2KCl + 3H_3AsO_4 + 4$$

$SnCl_2$, $SbCl_3$, $FeCl_2$, Zn (Fe, Sn, &c.), in the presence of dilute
also reduce chromates or dichromates. The reduction is quite e
effected by most organic substances, such as alcohol, in the presen
HCl, in which case the alcohol is oxidised to aldehyde, acetic e
and other products. $K_2Cr_2O_7$ is much used for this kind of oxida
both in the laboratory and on a manufacturing scale.

Reactions for CrO_3 produced by Double Decomposition.

Chromates of K, Na, Li, Cs, Rb, NH_4 (Ca, Sr), Mg are f
soluble in water. Others are much less soluble, none are absolu
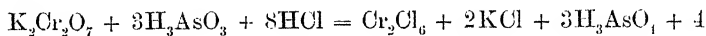insoluble, and all chromates dissolve readily in dilute nitric acid

$BaCl_2$, added to a solution of a normal chromate (or dichrom
gives a light lemon-yellow precipitate of barium chromate, BaC
even in very dilute solutions, as it is very insoluble in water, al
acetic acid, soluble in dilute nitric or hydrochloric acid, and pre
tated again by ammonia solution.

$Pb(C_2H_3O_2)_2$ (lead acetate) gives a fine lemon-yellow precipita
lead chromate, $PbCrO_4$, soluble in KHO, sparingly soluble in d
nitric, insoluble in acetic acid. The neutral salt is converted u
digestion with alkalis into a basic red chromate, $PbCrO_4,PbO$.

$AgNO_3$ (silver nitrate) gives a dark purple-red precipitat
silver chromate, Ag_2CrO_4, soluble in nitric acid and ammon
hydroxide. From weak acid solutions silver dichromate, Ag_2Cr_2O
precipitated.

$Hg_2(NO_3)_2$ (mercurous nitrate) gives a dark brick-red l
precipitate of Hg_2CrO_4,Hg_2O, corresponding to the lead-salt, w
on ignition is converted into oxygen, mercury vapour, and fi
divided green, Cr_2O_3. (Method of separating chromic acid f
chromic oxide.)

On bringing together a little chromic acid with hydrogen
oxide, O_2H_2, solution, a deep indigo-blue colour is produced, ov
probably to the formation of a perchromic acid.

A solution of perchromic acid decomposes, however, rapidly v
evolution of oxygen, leaving H_2CrO_4 and Cr_2O_3; its constitutio
yet unknown. A solution in ether is more stable than an aqu
solution. It is obtained by adding ether to a very dilute (a
solution of O_2H_2, and then a drop of dilute solution of a chromat
dichromate. On shaking, the ether takes up the perchromic acid,
acquires an intensely blue colour. Mere traces of CrO_3 can be
covered in this manner, or, *vice versa*, very small quantities of O
This is perhaps the most reliable test for H_2O_2.

FIG. 64.—Aluminium bronze (Cu 90 per cent., Al 10 per cent.), cast in sand.   (× 75.)
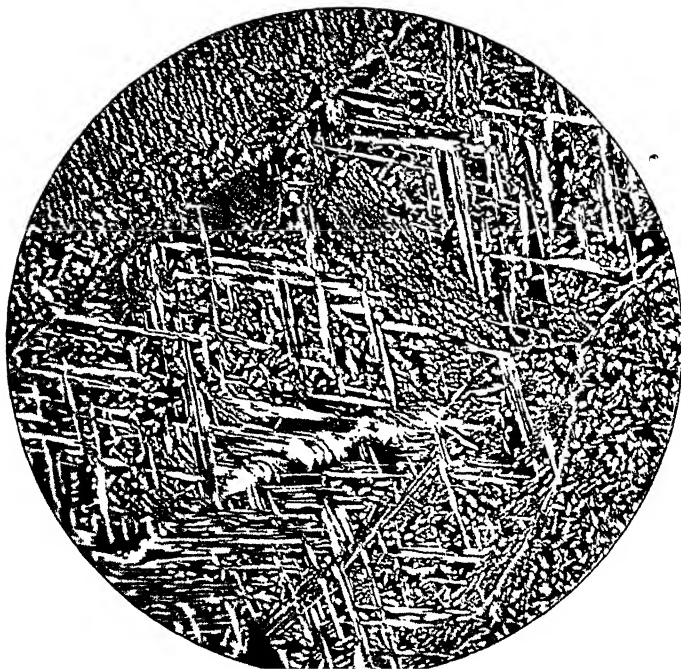
ALUMINIUM, Al^{iii} and ^{iv}.—Is one of the metallic elements which occur most abundantly in nature in the form of the oxide. Ruby, sapphire, emery are almost pure Al_2O_3. It is a constituent of many minerals, in combination with silica, with sulphuric, phosphoric, and other acids; and in the form of fluoride in cryolite and topaz. The element in the metallic state is not known free in nature, but is obtained by heating its chloride with sodium, also by several electrolytic methods on fused aluminium fluoride, with bauxite, &c. &c. It is white, with a decided blue tint, has nearly the hardness of copper, is very malleable and ductile, and is practically permanent in air. Water scarcely acts upon it, but most diluted mineral acids dissolve it readily, as do all alkaline liquids, but not ammonium hydroxide. Solutions of chlorides, and therefore sea-water, act upon it. Its atomic weight $= 27·01$; specific gravity, $2·60$; melts at about $800°C.$, and is not appreciably volatile at that temperature. It is an excellent conductor of heat and electricity, and forms alloys with most other metals. Its specific heat is very great—$i.e.$, $·2143$.

Aluminium, in addition to being employed in the compact form, is also valuable in the state of powder (obtained by pounding the metal when at a temperature just below fusion), which is used for paint and for reducing many oxides, as Cr_2O_3, &c., to the metallic state. In many of these reactions an exceedingly high temperature is produced, so that the product, although infusible in all ordinary furnaces, is completely melted. This fine powder forms, with some compounds rich in oxygen, highly explosive mixtures, which are used for some military purposes and for flashlight photography.

Alloys of the metal are numerous. Aluminium-bronze—copper 90 per cent., aluminium 10 per cent.—compares well with mild steel for tensile strength, &c. As it removes oxygen from CO, it is frequently added to steels at the moment of casting to decompose the dissolved gas and give sound castings. Lead is almost the only metal with which it does not unite.

Experiments.

I. Aluminium, in foil or wire, heated in air, melts; the surface becomes dull owing to a very thin layer of white oxide. The oxidation is very slow, as this layer of oxide seems to protect the underlying metal.

II. Heated with sulphur, no action takes place until a full red heat is attained. A little sulphide is formed, but the action is slight and never quite complete in an ordinary glass tube.

III. HCl acts very rapidly, hydrogen being evolved. On evaporating the solution to dryness the hydrate or oxide is left as a white powder. The chloride in solution is probably $AlCl_3 3HCl$, which is decomposed by the water on evaporation into $Al(HO)_3$ and HCl.

Sulphuric acid, dilute, acts slowly. A white, indistinctly crystalline sulphate is left, $Al_2 3SO_4$.

Nitric acid acts most slowly; when concentrated scarcely at all. On evaporating, a white hydrate is left, all the nitric going off with the water.

IV. Alkalies, KHO, NaHO, dissolve the metal and 'liberate hydrogen. The action on gently heating becomes somewhat violent. So-called aluminates are formed, as $Al_2O_3 3K_2O$.

Ammonia has no action on the metal or oxide.

The oxide dissolves in soda unless it has been very strongly ignited or it be the native form, as corundum, emery, or ruby, or sapphire. These forms are also insoluble in acids.

Dry Reactions.

Alumina, when heated on charcoal, is distinguished from other oxides by its property of glowing brightly, and assuming a beautiful sky-blue colour, after being moistened with a solution of cobaltous nitrate and again heated strongly, owing to its forming with the cobalt oxide a salt—cobaltous aluminite. This test is not always decisive, and becomes inapplicable when coloured oxides, such as Fe_2O_3, MnO, &c., are present. Also many phosphates and borates give a blue which to the unpractised eye appears the same.

Reactions in Solution.

Soluble salts of aluminium, as alum, $Al_2 3SO_4, K_2SO_4 24OH_2$, may be used for testing. There are comparatively few soluble ones in use.

$(NH_4)_2S$ gives a white gelatinous precipitate of aluminic hydroxide, $Al_2(HO)_6$, sulphuretted hydrogen being evolved, thus: $(NH_4)_2Al_2(SO_4)_4 + 3(NH_4)_2S + 6OH_2 = Al_2(HO)_6 + 4(NH_4)_2SO_4 + 3SH_2$.

KHO or NaHO * precipitates the hydroxide, readily soluble in excess, forming a compound, sodium aluminate, $Al_2Na_6O_6$, which is reprecipitated by excess of ammonium chloride, or by ammonia after neutralisation of the alkali by hydrochloric acid. The alkaline solution is not precipitated by ammonium sulphide. (Method of separation of Al from Fe^{iv}.)

NH_4OH precipitates the hydroxide, somewhat soluble in excess, when cold insoluble in the presence of much ammonium chloride, and on boiling.

Na_2CO_3 or K_2CO_3 precipitates basic carbonate of uncertain composition.

$BaCO_3$ precipitates $Al_2(HO)_6$ slowly, but completely, even cold, mixed with a basic salt. Carbon dioxide escapes.

Sodium hydrogen phosphate gives a bulky white precipitate of aluminic phosphate, $Al_2P_2O_8$, insoluble in ammonium hydroxide and chloride; soluble in KHO or NaHO, and in acids, but not in hot acetic acid. (Distinction of Al_2O_3 from aluminic phosphate.) Alkali acetates precipitate $Al_2P_2O_8$ from its solution in mineral acids. The

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* Potassium and sodium hydroxides are mostly contaminated with alumina, derived during the manufacture from porcelain vessels, and it is therefore necessary to employ pure NaHO (prepared in silver or nickel vessels) for the separation of Fe and Al. It must also be recollected that NaHO acts, in the course of an ordinary analysis, destructively upon porcelain and glass vessels, dissolving both silica and alumina, which give similar reactions with ammonia and its salts.

presence of citric acid, but not of tartaric acid or of sugar, prevents its precipitation. NH_4Cl precipitates the phosphate from its soda solution.

In order to decompose aluminium phosphate (as in the mineral wavellite) it is best to fuse the finely powdered mineral with $1\frac{1}{2}$ parts of finely divided SiO_2 and 6 parts of Na_2CO_3 in a platinum crucible for about half an hour.   The mass is digested for some time with water, and acid ammonium carbonate, NH_4HCO_3, added in excess; it is then filtered and washed.   The residue consists of aluminic and sodium silicates; the solution contains the sodium phosphate.   Dissolve the residue in dilute hydrochloric acid, and evaporate to dryness to separate the silica, and filter.   The filtrate may be tested for Al in the usual way.

Alumina occurs mostly in minerals which are not soluble in acids. Boiling with concentrated sulphuric acid attacks many; all are, however, decomposed by fusion with $KHSO_4$, or with fusion mixture, after which they are soluble either in water or in dilute hydrochloric acid.

Powder up some porcelain very finely, and fuse for half an hour in a platinum crucible with four times its weight of fusion mixture. Extract with water.   Transfer both the soluble and insoluble portion—consisting of alkali aluminate—to a porcelain dish, acidulate with hydrochloric acid, and evaporate to dryness.   Take up with a few drops of concentrated hydrochloric acid and hot water, and filter; wash the insoluble SiO_2 well with hot water.   The filtrate contains the aluminium as chloride, from which it can be precipitated by ammonium hydroxide as usual.

Aluminic silicate is often found in nature associated with potassium or sodium silicate, as in felspar and albite.   In order to test for potassium and sodium, alkali salts must, of course, be carefully avoided.   This can be done by making use of hydrofluoric acid, or by heating in a platinum crucible or on foil with CaO or with calcite, $CaCO_3$.

Introduce a small quantity of finely powdered felspar into a platinum * crucible or dish; cover with liquid hydrofluoric acid, and evaporate at a gentle heat in a closet or under a hood which is connected with the chimney.   HF attacks the SiO_2, forming silicon fluoride, SiF_4—a volatile compound—and leaves the aluminium and potassium behind as fluorides, which dissolve in dilute hydrochloric acid :

$$K_2Al_2Si_6O_{16} + 32HF = 6SiF_4 + 2KF + Al_2F_6 + 16OH_2.$$
$$\text{Volatile.}$$

The decomposition is generally only completed after two or three evaporations with HF.

Mix the fine powder of felspar with either powdered calcite or CaO and heat strongly—best in a covered crucible—for thirty minutes. On treating with HCl and evaporating to dryness the SiO_2 becomes insoluble and Al, Ca, K may be taken up by water as chlorides.

* With care, a leaden dish will do.

N.B.—The separation of the metals of Group III. is surrounded by some difficulties which arise from the possible simultaneous precipitation of

1st. Sulphides, NiS, CoS, MnS, ZnS, FeS,
2nd. Hydroxides, $Cr_2(HO)_6$, $Al_2(HO)_3$, and
3rd. Phosphates of Cr, Al, Ba, Sr, Ca, Mg,

and it is therefore well always to ascertain by a special experiment whether phosphoric acid is present or not in the solution under examination.

This can readily be done by adding to a small part of the solution a little concentrated nitric acid and a solution of ammonium molybdate.* A yellow precipitate is obtained, especially on gently heating, showing the presence of phosphoric acid. If no precipitate is obtained, phosphates are absent.

(a) *Phosphoric acid is absent.*—This is indicated if the original substance dissolved readily in water. If insoluble in water, but soluble in dilute acids, phosphoric acid may likewise be absent from the substance.

It would appear at first sight that the behaviour of the five sulphides and two hydroxides with ammonium chloride and ammonium hydroxide, sodium or potassium hydroxide, or dilute acids (*e.g.*, HCl), would enable the members of this group to be separated, or several of them, from each other. It has been shown, for example, that—

1st. Ni, Co, Mn, Zn are not precipitated by ammonium hydroxide from a hot solution containing large excess of NH_4Cl, whilst $Fe_2(HO)_6$, $Cr_2(HO)_6$, and $Al_2(HO)_6$ are precipitated. It has, however, been found that the mode of separation, based upon this solvent property of ammonium chloride, gives but imperfect results, since the $Fe_2(HO)_6$ carries down varying quantities of other oxides, especially on exposure of the solution to the air, when higher oxides of manganese and cobalt are formed, which are not soluble in ammonium chloride. Small quantities of Ni, Co, Mn, and Zn may thus be overlooked altogether. It is only by redissolving the precipitate and reprecipitating several times, as long as the ammoniacal filtrate gives a precipitate with sulphuretted hydrogen, that iron can be completely separated from manganese, &c., in this manner.

With these precautions, however, it is mostly possible to separate the metals of this group from each other by first precipitating ferric, chromic, and aluminic hydroxides by means of NH_4Cl and NH_4OH, and then from the filtrate the sulphides of Ni, Co, Mn, and Zn by means of SH_2 or $(NH_4)_2S$.

2nd. That Zn, Al, and Cr are precipitated by KHO or NaHO, but are soluble in excess, whilst the other metallic hydroxides are insoluble. From this it would appear that these three metals can be separated by means of the fixed alkali hydroxides. But it has been found here again that $Fe_2(HO)_6$, $Ni(HO)_2$, $Co(HO)_2$, $Mn(HO)_2$ carry down appreciable quantities of $Zn(HO)_2$, and more especially

* For the preparation of this reagent see Appendix, "Reagents."

the $Fe_2(HO)_6$ precipitate of $Cr_2(HO)_6$, and that a complete separation cannot be effected by precipitation with KHO or NaHO.

3rd. Cold dilute hydrochloric acid does not dissolve CoS or NiS to any great extent, but dissolves the other sulphides and hydrates. This method, if practised with care, gives good results, small traces only of CoS and NiS being generally dissolved out. But as it leaves the iron, aluminium, and chromium still to be separated from manganese and zinc, no saving of labour is effected thereby in the separation of these seven metals.

Finely divided, freshly precipitated barium carbonate is a reagent which separates the lower oxides—viz., ZnO, MnO, NiO, CoO (this latter not quite so perfectly, except in the presence of much ammonium chloride)—from the higher oxides—viz., Fe_2O_3, Al_2O_3, and Cr_2O_3. The metals should be first obtained as chlorides.

The examination of the precipitate produced by barium carbonate is based upon—

1st. The solubility of $Al_2(HO)_6$ in sodium hydroxide.

2nd. The conversion of Cr_2O_3 into CrO_3 by fusion with sodium carbonate and nitre, or by boiling with ClNaO, or with PbO_2 in an alkaline solution.

The examination of the filtrate is based upon—

1st. The solubility of $Zn(HO)_2$ in sodium hydroxide.

2nd.   ,,   MnS in acetic acid.

3rd. The formation of soluble $K_6Co_2Cy_{12}$ and the precipitation of Ni as black $Ni_2(HO)_6$ by sodium hypochlorite, or hypobromite.*

Directions for the separation of these seven metals will be found in the analytical tables under Group IIIA.

(β) *Phosphoric acid is present.*—The original substance was either insoluble or only partially soluble in water, but soluble in hydrochloric acid. In this case NH_4Cl and NH_4OH† produce a precipitate before $(NH_4)_2S$ is added. If $(NH_4)_2S$ is added without filtration after the addition of NH_4OH, the precipitate may possibly consist of NiS, CoS, MnS, ZnS, FeS, $Al_2(HO)_6$, $Cr_2(HO)_6$, as well as the phosphates of (Cr), Al, Mg, Ca, Sr, Ba.

Ammonium chloride and hydroxide precipitate Ni, Co, Mn, Zn, and Fe phosphates without decomposition. Ammonium sulphide converts the phosphates of Ni, Co, Mn, Zn, and Fe into sulphides and ammonium phosphate, and this could then act upon any soluble salts of Ba, Ca, Sr, Mg, and convert them into phosphates, although they were not as phosphates in the original mixture.

An example will make this clear. Supposing that the substance under examination consists of barium carbonate and calcium and ferric phosphates, $BaCO_3, Ca_3P_2O_8$ and $Fe_2P_2O_8$. On dissolving in hydrochloric acid, barium chloride is formed, and the calcium and ferric phosphates are dissolved without decomposition. On adding

* Instead of NaOCl bromine water may generally be used. In an alkaline solution a hypobromite, as NaOBr, is formed. The oxidising action is just the same.

† If ammonium chloride and ammonia should give no precipitate, it is obvious that no phosphates and no Fe, Al, and Cr need be looked for.

NH_4Cl and NH_4OH, a yellowish-white precipitate of $Fe_2P_2O_8$ and $Ca_3P_2O_8$ is obtained, whilst $BaCl_2$ is not precipitated. On adding, however, $(NH_4)_2S$ as well as the ammonium chloride and ammonia to the solution, $Fe_2P_2O_8$ is decomposed into ferrous sulphide and ammonium phosphate, which latter, by acting upon the $BaCl_2$, would precipitate barium phosphate.

In order to avoid this, the precipitate produced in Group III. by NH_4Cl and NH_4OH, which contains for the most part the whole of the phosphates, is filtered off, and $(NH_4)_2S$ added to the filtrate only.

The ammonia precipitate is dissolved in a little dilute HCl, nearly neutralised with Na_2CO_3, and an excess of a solution * containing sodium acetate and acetic acid is added. The phosphates of iron, chromium, and aluminium are precipitated. Any phosphates of the alkaline earths left undecomposed by the ferric chloride already present in the solution are held in solution by the acetic acid. To the filtrate add Fe_2Cl_2, drop by drop, as long as a precipitate † is obtained, and till the colour of the supernatant liquid becomes distinctly reddish. Digest at a gentle heat; allow to subside, and filter. In this manner the whole of the phosphates of the alkaline earthy bases are decomposed, with formation of the $Fe_2P_2O_8$, insoluble in acetic acid (which precipitate may be neglected), and chlorides of Mg, Ba, Sr, Co which remain in solution, together with the chlorides of Ni, Co, Mn, Zn. The whole of the phosphoric acid having thus been removed, the metals that were originally present as phosphates may be detected in the usual way.

It may be of interest to ascertain whether oxalates of Ba, Sr, and Ca (which are destroyed by evaporation with nitric acid and ignition, before proceeding to Group III.), were present in the original mixture, in which case the evaporation to dryness and ignition must be omitted.

The precipitate produced in Group III. by ammonium chloride and hydroxide alone contains the oxalates as well as the phosphates of the alkaline earthy bases, and possibly also gelatinous silica. The oxalates are decomposed by gently igniting the precipitate, and are converted into carbonates. The ignited mass effervesces strongly on extraction with dilute hydrochloric acid. When the solution is evaporated to dryness and again taken up with dilute HCl, the silica, if present, is rendered insoluble, and may be separated by filtration. To the acid solution, which may possibly contain phosphates of Mg, Ca, Sr, and Ba, as well as chlorides of the bases, present before ignition as oxalates, add NH_4Cl and NH_4OH and filter off. The filtrate contains the chlorides of Ba, Sr, and Ca, and

* For the preparation of this reagent see Appendix.

† If any phosphates of the alkaline earthy bases be left, Fe_2Cl_6 should produce a yellowish white precipitate when adedd to a portion of the acetic acid solution ; if not, no ferric salt need be added to the main portion of the filtrate. (The presence of iron, other than phosphate, is generally indicated by the reddish or ferric acetate colour of the filtrate.) In this case Al and Cr, as well as the metals of the alkali earths, will still have to be looked for in the filtrate.

is tested separately according to Table IV.   All bases so discovered must have been present originally as oxalates.

The separation of the individual members of this group is based upon :

1st. The insolubility of the phosphates of Fe, Al (and Cr) in acetic acid in the presence of an alkali acetate.

2nd. The separation of the whole of the phosphoric acid which is in combination with the alkaline earthy bases, by means of Fe_2Cl_6, in an acetic solution.

All other operations are identical with those already described.

Phosphates may be decomposed in another way, depending on the fact that almost all phosphates, excepting those of molybdenum and tin, are soluble in strong nitric acid.   When any phosphate is mixed with tin, in filings, or finely granulated, and then covered with moderately strong—50 per cent.—nitric acid, a violent action takes place between the Sn and the acid, resulting in the formation of a stannic hydroxide—so-called meta-stannic acid.   The phosphates are at the same time dissolved by the nitric acid.   This stannic hydroxide (or acid) combines with the P_2O_5 of the phosphates, forming a compound quite insoluble in strong or dilute nitric, but decomposed by hydrochloric acid.

The process is best carried out by evaporating the filtrate, after passing SH_2, in which phosphates have been found, to dryness or nearly so, adding a few grams of tin filings, and covering with moderately strong HNO_3, stirring well, and allowing to evaporate on a sand-bath or wire gauze over a flame nearly to dryness.   After cooling dilute HNO_3 is added, the solution warmed and filtered.   All the bases will be found in solution as nitrates, and the P_2O_5 will be retained in the white tin oxide residue.   Chlorides should be absent.

Before proceeding the nitric acid filtrate must be tested for P_2O_5 by ammonium molybdate.

Although the metals of Group III. arrange themselves very well for analytical purposes *as* a group, there are considerable differences amongst them in other respects.   Fe, Ni, Co, Zn are easily reduced from their oxides, Fe_2O_3, NiO, CoO, ZnO, by carbon or CO.   MnO is not so easily reduced, and Al_2O_3 and Cr_2O_3 are practically not reduced, by C or CO alone at any temperature.   The easiest method of reduction in these cases is from their chlorides by sodium or magnesium or in the electric arc.   By the simultaneous action of Cl and C on the oxides, as $Al_2O_3 + 3C + 3Cl_2 = Al_2Cl_6 + 3CO$, the dry chlorides are produced, and these may be decomposed by sodium. Cr_2O_3 behaves in exactly the same manner.

The metallic character of chromium, measured by the few salts it forms with acids, is less than that of the other elements in the group.   The sulphides also of Cr and Al are not producible by wet processes, whilst all the other metals readily form sulphides from aqueous solutions of their salts.   Nickel and cobalt might almost be looked upon, from the behaviour of some of their salts, oxides, &c., as being enantiomorphous bodies.

With the exception of zinc and aluminium, all these elements have high melting-points. Their oxides are all almost infusible substances. The chlorides are all fusible and volatile; $ZnCl_2$ most easily, followed by $AlCl_3$ and $CrCl_3$. $FeCl_3$, $NiCl_2$, $CoCl_2$, and $MnCl_2$ melt but do not vapourise easily, excepting in a current of chlorine gas. Aluminium and chromium chlorides are scarcely, if at all, reduced by hydrogen at a red heat. The others are moderately easily reduced, $MnCl_2$ being the most difficultly reducible.

The carbides of Al, Cr, Fe, and perhaps also of Mn, when decomposed by water, or HCl, give hydrocarbons of the paraffin series as well as acetylene.

Al, Cr, and Fe show a strong tendency to form alums, whilst Ni, Co, and Zn do not form this class of salt, and Mn, in this respect, seems to fall between the two sets of metals.

CHAPTER XII.

REACTIONS OF THE METALS OF GROUP II.

THIS group comprises the metals mercury, lead, bismuth, copper, cadmium, arsenic, antimony, tin (gold and platinum), which are precipitated from acid solutions (HCl) by means of sulphuretted hydrogen.

As an exercise mix together solutions of $Bi(NO_3)_3$, $HgCl_2$, $CuSO_4$, $CdCl_2$, As_2O_3 (dissolved in HCl), $Pb(NO_3)_2$, $SbCl_3$, $SnCl_2$, and $SnCl_4$, and pass a current of SH_2, without first filtering off the white precipitate which is produced. Filter; pass the gas again through the clear filtrate, to make sure that the metals have been entirely precipitated. Wash the precipitate with hot water; remove a portion from the filter and boil it with a little yellow ammonium sulphide, and filter off. A black residue is left, consisting of HgS, PbS, Bi_2S_3, CuS, CdS. The solution contains As_2S_3, Sb_2S_3, SnS, and SnS_2 dissolved in the ammonium sulphide.* This can be shown by acidulating with dilute hydrochloric acid, when a yellowish precipitate comes down,† consisting of the sulphides of As, Sb, Sn.

This shows that Group II. may be divided, by means of ammonium sulphide or other alkali sulphide, into two portions.

The name sulphide, in its widest sense, is given to all compounds into which sulphur enters as the electro-negative element. A striking analogy is observable between oxides and sulphides. There is a certain class of sulphides which resembles metallic oxides or bases; another class which plays the part of oxy-acids.‡ Sulphides are therefore divided into sulpho-bases and sulpho-acids. To the latter belong the sulphides of H, As, Sn, Sb (Pt, Au); to the former the sulphides of many metals, especially such of the metals as constitute powerful bases (K, Na, NH_4, Ba, Ca, &c.). An electro-positive element, which forms with oxygen an oxide, combines generally also with the same number of sulphur atoms, to form a corresponding

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* Potassium or sodium-hydrosulphides are nearly as efficient as the ammonium sulphide. It is noticed here, and later, that K and Na sulphides exert a slightly different solvent action on the sulphides of the group to that exerted by ammonium sulphide. There is no doubt that the solubility of these sulphides is due to the formation of a definite double-sulpho salt.

† Yellow ammonium sulphide converts SnS into SnS_2.

‡ Peroxides have their analogues in persulphides. Both can act as acids or electro-negative groups to others with less oxygen or sulphur.

sulphide, in which the sulphur is performing similar functions to oxygen.

The resemblance in the constitution of these oxygen and sulphur compounds is further borne out by the analogy in their solubility and alkaline reaction :

	Oxy-bases.		Sulpho-bases.
OK_2	Potassium oxide, alkaline and soluble.	SK_2	Potassium sulphide, alkaline and soluble.
$O(NH_4)_2$	Ammonium oxide ,,	$S(NH_4)_2$	Ammonium ,, ,,
ONa_2	Sodium ,, ,,	SNa_2	Sodium ,, ,,
BaO	Barium ,, ,,	BaS	Barium ,, ,,
CaO	Calcium ,, ,,	CaS	Calcium ,, ,,
FeO	Ferrous oxide, no reaction, insoluble.	FeS	Ferrous ,, no reaction, insoluble.
ZnO	Zinc ., ,,	ZnS	Zinc ,, ,,

	Oxy-anhydrides.		Sulpho- or thio-anhydrides.
As_2O_3	Arsenious anhydride.	As_2S_3	Arsenious sulphide, or sulph-arsenious anhydride.
As_2O_5	Arsenic ,,	As_2O_5	Arsenic sulphide, or sulphar-senic anhydride.
Sb_2O_3	Antimonious ,,	Sb_2S_3	Antimonious sulphide, or sulphantimonious anhydride.
Sb_2O_5	Antimonic ,,	Sb_2S_5	Antimonic sulphide, or sulph-antimonic anhydride.
SnO_2	Stannic ,,	SnS_2	Stannic sulphide, or sulpho-stannic anhydride.

	Oxy-acids.		Sulpho- or thio-acids.
H_3AsO_3	Arsenious acid.	H_3AsS_3	Sulpharsenious acid.
H_3AsO_4	Arsenic acid.	H_3AsS_4	Sulpharsenic acid.
H_3SbO_3	Antimonious acid.	H_3SbS_3	Sulphantimonious acid.
H_3SbO_4	Antimonic acid.	H_3SbS_4	Sulphantimonic acid.
$HSbO_3$	Metantimonic acid.	$HSbS_3$	Sulphometantimonic acid.
H_2SnO_3	Stannic acid.	H_2SnS_3	Sulphostannic acid.

To this list might be added CO_2 and CS_2, which form carbonates and sulphocarbonates respectively, and some others. The analogy here is most complete. K_2COS_2 is an intermediate compound between the ordinary alkali carbonate and K_2CS_3, the real sulpho-, or thio-, carbonate.

Sulpho-salts are obtained by the mutual action of a sulpho-acid and a sulpho-base upon each other.

Sulphides soluble in water, comprising the sulphides of the alkalis and alkaline earthy metals, are divided into normal sulphides, such as SK_2, $S(NH_4)_2$, SNa_2, BaS ; into sulphydrates (acid sulphides), such as SKH, SNH_4H, BaH_2S_2 ; and *polysulphides*, such as S_2H_2, S_5K_2, $S_5(NH_4)_2$.* The aqueous solutions of the normal and acid sulphides

* The composition of the so-called polysulphides has not been made out with certainty. Indeed, no scientific examination has as yet been made of them. Melted sulphides seem to dissolve a large amount of sulphur, which may be retained in solid solution, or they are very likely the analogues of sulphites and sulphates in which sulphur is acting the part played by oxygen in true sulphites and sulphates, thus ; K_2SO_4 : K_2SS_4, and $Na_2S_2O_7$: $Na_2S_2S_7$, &c.
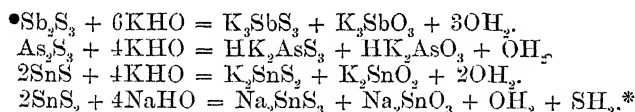
are colourless, and give off SH_2 when treated with dilute hydrochloric acid, without separation of sulphur.   Solutions of the polysulphides are yellow, or yellowish brown, and when treated with hydrochloric acid give off sulphuretted hydrogen, with separation of white (or precipitated) sulphur.   In some cases hydrogen persulphide, H_2S_2, the analogue of H_2O_2, is formed.   The number of sulpho-salts known is small compared with the salts of oxy-acids, and they are far less stable than ordinary oxy-salts.   The number of sulpho-acids is principally restricted to the acids enumerated above, and these again combine mostly only with the soluble sulphides possessed of an alkaline reaction ; or, if combined with the sulphides of the heavy metals, as in certain cases, they are somewhat easily decomposed by chemical agencies.   Some are certainly found as minerals.

The following is a list of some sulpho-salts compared with the corresponding oxy-salts :

| Oxy-salts.		Sulpho-salts.	
Na_2SnO_2	Disodium stannite.	Na_2SnS_2	Sodium sulphostannite.
Na_2SnO_3	Disodium stannate.	Na_2SnS_3	Sodium sulphostannate.
K_3AsO_3	Tripotassium arsenite.	K_3AsS_3	Potassium sulpharsenite.
Na_3AsO_4	Trisodium arsenate.	Na_3AsS_4	Sodium sulpharsenate.
$KSbO_2$	Potassium metantimonite.	$KSbO_2$	Potassium metasulphantimonite.
$KSbO_3$	Potassium metantimonate.	$KSbO_3$	Potassium metasulphantimonate.

Treat another portion of the above SH_2 precipitate with NaHO or KHO and filter off.   A black residue is likewise left, and on adding dilute HCl to the filtrate As_2S_3, Sb_2S_3, SnS, and SnS_2 are reprecipitated.

This shows that the *hydroxides* of the alkali metals dissolve a portion of the sulphides precipitated by SH_2.   The following equations explain the action of the alkali hydroxides :

$$Sb_2S_3 + 6KHO = K_3SbS_3 + K_3SbO_3 + 3OH_2.$$
$$As_2S_3 + 4KHO = HK_2AsS_3 + HK_2AsO_3 + OH_2.$$
$$2SnS + 4KHO = K_2SnS_2 + K_2SnO_2 + 2OH_2.$$
$$2SnS_2 + 4NaHO = Na_2SnS_3 + Na_2SnO_3 + OH_2 + SH_2.*$$

These may be called mixed reactions.

Addition of hydrochloric acid reprecipitates the sulphides, thus :

$$K_3SbS_3 + K_3SbO_3 + 6HCl = Sb_2S_3 + 6KCl + 3OH_2.$$
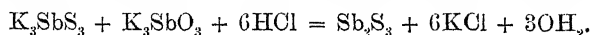
Hence the metals which are precipitated by SH_2 in Group II. can be subdivided by means of ammonium sulphide or sodium or potassium hydroxides into—

A. Metals whose sulphides act as sulpho-bases—viz., the sulphides of Hg, Pb, Bi, Cu, and Cd.   These are insoluble in ammo-

* No SH_2 is given off in this reaction.   As excess of NaHO is always used, it may be represented : $2SnS_2 + 5NaHO = Na_2SnS_3 + Na_2SnO_3 + 2OH_2 + NaHS.$

nium sulphide (HgS dissolves to some extent in potassium or sodium sulphide; CuS is somewhat soluble in ammonium sulphide).

B. Metals whose sulphides act as sulpho-acids—viz., the sulphides of As, Sb, Sn (Au, Pt).

GROUP II. SUBDIVISION A.

(1) **MERCURY,** Hg''.—Occurs native, but is chiefly obtained from cinnabar or mercuric sulphide, HgS, by heating with lime or iron turnings in a distilling apparatus or retort. The element is liquid at ordinary temperatures and down to about $-40°$ C., at which temperature it crystallises. Both the solid and liquid states exhibit a metalline lustre and colour like silver. It is malleable whilst solid. It has an atomic weight of $199·71$, generally taken as 200. Specific gravity $= 13·55$ in the liquid and $14·19$ in the solid state. The solid melts at $-38·50°$ C. and boils at $357·25°$ C. under a pressure of 760 mm. It does not tarnish appreciably in the air, but is very slowly oxidised when gently heated to about $300°$ C. in an atmosphere of oxygen. Ozone acts more rapidly and at low temperatures. Nitric acid acts readily upon it, even when cold; sulphuric only when heated and strong. Hydrochloric acid or alkalies have no action. It combines energetically with chlorine, bromine, iodine, and sulphur, also with sodium and potassium and some other metals, forming amalgams, but not with iron, platinum, nickel, cobalt, or aluminium.

This property of mercury has received an important application in the extraction of gold and silver from poor ores by the so-called amalgamation process, in which the mercury can be separated again by distillation, the gold or silver being left behind.

When cinnabar, HgS, is roasted in the air, the sulphur is oxidised to SO_2 and metallic mercury sublimes.

Hydrogen and carbon, copper, tin, zinc, &c., reduce HgS at a high temperature, forming with the sulphur SH_2, CS_2 (carbon disulphide), CuS, &c. The native HgS is, however, best reduced by the action of strong bases, such as lime or soda.

Mix a little cinnabar with dry sodium carbonate, and heat in a little tube, sealed up at one end, or blown into a small bulb. Metallic mercury sublimes and forms a mirror in the cold part of the tube; the sulphur is retained by the alkali metal.

Mercury salts, when heated by themselves, out of contact with the air, volatilise or sublime, either without decomposition, such as $HgBr_2$, $HgCl_2$, Hg_2Cl_2, HgI_2, HgS, HgICN; or they are decomposed into oxide or metal, as HgN_2O_6, the nitrate, which gives $HgO + N_2O_4 + O$. Salts of mercury with fixed acids, as the phosphate or chromate, leave fixed residues of acid or oxide (Cr_2O_3).

Sulphates of mercury decompose on heating into SO_2, HgO, and O, and finally metallic Hg; carbonate into HgO and CO_2, and finally metal.

Probably the most delicate test for metallic mercury is a piece of metallic gold, a coin, which becomes whitened by an exceedingly small amount of Hg when suspended in its vapour or when the substance moistened with HCl is rubbed on the gold.   Some silver salts, as the sulphate or phosphate, will absorb mercury vapour or the vapour of volatile mercury compounds.   Bright metallic copper comes next in delicacy in showing this test.   A drop of Hg placed on a piece of aluminium and just moistened with HCl starts a peculiar action on the aluminium.   White filaments of Al_2O_3 grow up like fungus from the metal.

An amalgam of 4 parts of tin and 1 part of mercury is employed in the manufacture of looking-glasses.

Mercury forms two series of salts, mercurous and mercuric.

In mercurous salts the element exhibits less extent of energy of combination than in mercuric salts.   As, for instance, mercurous oxide, Hg_2O, calomel, Hg_2Cl_2; and mercuric oxide, HgO, corrosive sublimate, $HgCl_2$.   In the former case it is supposed that the metal is in some way combined with itself as Hg—Hg or Hg—Hg, whilst

$$\underset{O}{\diagdown\diagup} \qquad \underset{Cl}{|} \quad \underset{Cl}{|}$$
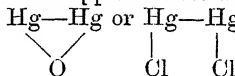
in the latter the whole extent of the energy of the mercury atom is expended on the substance with which it is combined.

Experiments.

I. Mercury when heated in a tube boils, evaporates, and condenses again in very small globules on the cool part, forming a mirror. After heating for some hours in air the surface lustre becomes less, but no appreciable oxidation takes place in the short time of an experiment.

II. Heated with sulphur, a black solid is formed which sublimes black.   On rubbing with a hard substance it becomes somewhat reddish.   It is HgS.

III. HCl has no action.

H_2SO_4, when boiling and strong, dissolves it, forming sulphate and liberating SO_2. $Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2$.   Crystals are obtained on cooling the acid solution.

Nitric acid acts most readily.   Oxides of N are evolved and the nitrate, $Hg(NO_3)_2$, crystallises out as the liquid cools.   On heating this nitrate oxides of nitrogen are given off and HgO left, which also decomposes into Hg and O.

Ammonia and alkalies have no action on the metal.

IV. Iodine combines very readily.   The HgI_2 formed sublimes yellow, generally, and becomes pink on rubbing.

V. Add a few clean filings of lead or zinc or tin to a few globules of mercury on a watch-glass.   The liquid mercury becomes thick and pasty by combination with the solid metal.

Reactions in Solution.

Mercury readily dissolves even in cold nitric acid, forming mercurous nitrate if the mercury is in excess, and mercuric nitrate if the

acid is in excess and hot.   These salts have the composition, or can be represented as :

$$Hg_2(NO_3)_2 \quad \text{and} \quad Hg(NO_3)_2.$$

Mercurous   Mercuric
nitrate.   nitrate.
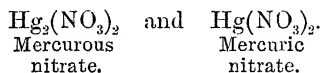
Mercurous oxide exhibits a tendency to combine with another atom of oxygen, or, when exposed to heat, to part with one atom of mercury, and the remainder to become converted into mercuric oxide. Hence mercurous salts act as reducing agents.

As mercurous chloride is insoluble, the reactions of mercurous salts will be considered in connection with the reactions of silver and lead in Group I.

In order to study the reactions of mercuric salts, a solution of mercuric nitrate, $Hg(NO_3)_2$, or mercuric chloride, $HgCl_2$ (corrosive sublimate), may be employed.   Not many mercury salts are *very* soluble and few are really insoluble in water.

SH_2 (group reagent) added to $HgCl_2$ gives a black precipitate of mercuric sulphide, HgS.   The precipitation is marked by characteristic changes of colour.   Accordingly, as sulphuretted hydrogen water is added in small quantities, or the gas passed slowly through the solution, it produces at first a perfectly white precipitate, and, on the addition of more SH_2, a yellow precipitate which passes through dirty yellow to brown, and becomes black only when excess of SH_2 has been added to the mercuric salt.   The white, yellow, or brown precipitate is a varying mixture of HgS and $HgCl_2$.   HgS is insoluble in nitric or hydrochloric acid and in yellow ammonium sulphide, alkali hydroxide or cyanide, soluble, however, in aqua regia and in potassium or sodium sulphide in the presence of sodium hydroxide, but insoluble in their sulphydroxides.   Long digestion with concentrated nitric acid converts the black HgS into a white substance, probably a compound of $2HgS + Hg_2(NO_3)_2$ (?).

Ammonium sulphide gives the same precipitate.

NaHO or KHO added in excess produces a yellow precipitate of mercuric hydroxide, $Hg(HO)_2$, insoluble in excess.

NH_4OH produces a white precipitate, from the chloride, of mercuric ammonium chloride, $NH_2Hg''Cl$, known as " white precipitate."

Sodium or potassium carbonates give a reddish-brown basic carbonate precipitate.

KI gives a bright red precipitate of mercuric iodide, HgI_2, soluble either in excess of potassium iodide or of the mercuric salt.

The solution contains $HgI_2 2KI$.   This is also known as a double salt, and is probably

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K
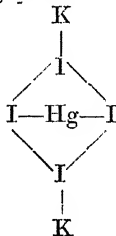
but no experimental evidence of this formula is to hand. The chloride $HgCl_2$ also forms a crystalline compound with $2KCl$, which may be similarly expressed :

$$
\begin{array}{c}
Cl-K \\
\diagup \quad \diagdown \\
Cl-Hg-Cl \\
\diagdown \quad \diagup \\
K-Cl
\end{array}
$$
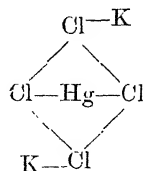
KCy gives with mercuric nitrate (not the chloride) a white precipitate consisting of cyanide and nitrate, soluble in excess, not decomposed by boiling with alkalies or alkali carbonates, but only by SH_2.

Mercuric salts are readily reduced to mercurous salts :

$SnCl_2$ (stannous chloride) gives with mercuric salts a white precipitate of mercurous chloride, Hg_2Cl_2, which, when boiled with excess of the reagent, is reduced to grey metallic mercury. On pouring off the solution and boiling the grey precipitate with HCl the mercury is obtained in little globules.

Ferrous sulphate reduces $Hg(NO_3)_2$, but not $HgCl_2$, to the metallic state.

Cu, Zn, Pb, Sn, Cd, and Fe precipitate metallic mercury from mercuric solutions, provided they are not too acid. They do not all act at the same rate.

If a strip of bright metallic copper be employed, a silvery white deposit of metallic Hg is obtained, which, when gently rubbed, shows a bright metallic lustre, and gives, after drying and heating in a dry and narrow test-tube, or bulb-tube, a sublimate of metal.

Generally mercuric salts are first reduced to mercurous salts, and finally to metallic mercury.

(2) **LEAD.**—Only a slight precipitate of PbS is for the most part obtained in Group II., since the greater part of the lead is removed in Group I. as $PbCl_2$. It happens frequently that this small quantity of lead is not precipitated by SH_2, on account of the solution being too acid (HCl), or too concentrated, in which case a little lead is found in Group III., and is often mistaken for some other metal. It is necessary, therefore, to dilute a portion of the filtrate from Group II. considerably, and to pass a current of SH_2 through in order to make sure of the presence of lead, especially so when lead has been discovered in Group I. ; and, if a precipitate be obtained, to pass the gas once more through the whole of the filtrate, after having diluted it considerably, or, better, neutralised it to some extent by adding ammonium hydroxide.

(3) **BISMUTH,** Bi''' and ^{v}.—This metal is found native ; also in combination with oxygen and sulphur, as bismuth ochre, Bi_2O_3, from the decomposition of bismuth glance, Bi_2S_3, and in the form of

sulpho-salts, as kobellite Bi_2S_3, 3PbS, and needle ore, Bi_2S_{3}, 2PbS, Cu_2S.

The metal is highly crystalline, brittle, of a white colour, with a red tinge. Atomic weight, 208·5; specific gravity, 9·80; melts at 266·8°, and boils between 1090° and 1450°.

It is not malleable at all, but powders up easily in a mortar.

Water and air have little or no effect at ordinary temperatures. It expands on solidifying from fusion similarly to ice. The metal is seldom employed alone, but is much used for alloys where fusibility is desired.

Experiments.

The metal may be melted in a test-tube.

I. Heated strongly in air, rapid oxidation takes place, fine coloured films pass over surface of melted metal, and a yellow or yellowish red oxide forms. The oxide is very fusible, and darkens on heating.

II. Heated with sulphur, combination takes place very readily to Bi_2S_3, a nearly black, crystalline, but non-volatile substance, which readily melts.

III. Hydrochloric scarcely acts at any temperature. Sulphuric acts very slowly, and only when concentrated and hot.

Nitric dissolves it most readily, with evolution of fumes of oxides of nitrogen and formation of $Bi3NO_3$, which readily crystallises when slightly evaporated in a dish. Ammonia and alkalies have no action either on metal or oxide.

The oxide dissolves readily in acids, and the solutions give crystals on evaporation. All the salts are colourless unless the acid be coloured.

Dry Reactions.

Salts of bismuth are reduced with ease on charcoal by the blow-pipe, covering the charcoal with an incrustation of oxide, orange-yellow while hot, lemon-yellow when cold, passing at the edges into a bluish white. The incrustation can be driven from place to place by either flame, without colouring the outer flame. (Distinction from lead.) Heated with borax or microcosmic salt, Bi_2O_3 gives beads which are yellowish when hot, and colourless when cold. All bismuth compounds can be reduced to the metallic state by heating on charcoal with sodium carbonate in the inner or reducing flame. The metallic bead is brittle. (Distinction from lead and silver beads.)

Reactions in Solution.

Bismuth dissolves readily in nitric acid, forming $Bi(NO_3)_3$. Other acids have little or no effect, and few real bismuth salts are known. (See its position in the "Natural Series.")

SH_2 (group reagent) gives a brownish black precipitate of bismuthous sulphide, Bi_2S_3, insoluble in dilute acids, in alkalies, and in alkali sulphides; soluble in concentrated nitric acid.

Alkali sulphides give the same precipitate.

KHO, NaHO, and NH_4OH produce a white precipitate of bismuthous hydroxide, $Bi(OH)_3$, insoluble in excess.

Alkali carbonates throw down a white bulky precipitate of basic carbonate $(BiO)_2CO_3$, in which the compound radical bismuthyl, BiO, takes the place of hydrogen. The precipitate is insoluble in excess.

$K_2Cr_2O_7$ gives a yellow precipitate of basic chromate $(BiO)_2Cr_2O_7$, readily soluble in dilute nitric acid, insoluble in potassium hydroxide. (Distinction from lead chromate.)

H_2SO_4 gives no precipitate. (Distinction from lead.)

KI produces a brown precipitate of bismuthous iodide, BiI_3, soluble in excess to a reddish solution.

KCy produces a white precipitate, insoluble in excess, soluble in acids.

Bismuthous salts are decomposed by water, a basic salt being precipitated. The addition of an acid redissolves the precipitate. This constitutes the most characteristic reaction for bismuthous salts. The salt most readily precipitated is the chloride $(BiCl_3)$. It can be prepared from the nitrate by precipitating the oxide first, and then filtering and dissolving the precipitate off the filter with hot dilute hydrochloric acid. Large excess of acid should be avoided.

OH_2 gives with $BiCl_3$ a white precipitate of bismuthous oxychloride, BiOCl, which is almost absolutely insoluble in water, but soluble in hydrochloric acid, from which it is reprecipitated on the addition of ammonium or sodium chloride. BiOCl is insoluble in tartaric acid. (Distinction from antimony.)

Metallic zinc precipitates bismuth as a black crystalline powder from its salts.

Bismuthous salts exhibit a strong tendency to form basic salts, showing that Bi is only a feebly positive element.

Other oxides of bismuth in addition to Bi_2O_3 are known, e.g., bismuthic oxide or anhydride, Bi_2O_5, and Bi_3O_7 and Bi'O no doubt also exist.

(4) **COPPER,** Cu''.—Is often found in the metallic state, and sometimes in considerable masses; frequently this "native" copper contains silver; also in combination with oxygen and sulphur, as red copper ore or ruby ore, Cu_2O, as vitreous copper or copper glance, Cu_2S, and indigo copper or blue copper, CuS; more frequently as copper pyrites, Fe_2S_3,Cu_2S, and variegated copper or horseflesh ore, $Fe_2S_3,3Cu_2S$, also as fahl ore, bournonite, &c.; in combination with carbonic acid, as basic carbonate, malachite, $CuCO_3.Cu(OH)_2$, and azurite, mountain blue, or copper azure, $2CuCO_3,Cu(OH)_2$; with sulphuric acid as blue vitriol, $CuSO_4,5OH_2$; with phosphoric acid, as phosphorocalcite, libethenite; with arsenious acid, as tennantite; with silicic acid, as dioptase, and others.

Copper is the only metal of a decided red colour. Its atomic weight $= 63.17$; specific gravity, 8.92; melts at 1054° C.

It is very tough and ductile, takes a fine polish or burnish, and is one of the best conductors of heat and electricity.

On exposure to clean air it oxidises very slowly at ordinary temperatures, but rapidly when heated to redness. The dirty air of towns, containing sulphur compounds, &c., attacks the metal rapidly. Water has no action on copper at any temperature, but most acids attack it, *especially if exposed to air* at the same time. Alkalies, including lime, and especially ammonia, also act upon it under *similar* circumstances.

Copper, on account of its malleability and comparatively high tensile strength and other physical properties, is much employed alone.

It is also the main component of alloys of great technical importance, such as brass, and a number of others designated generally by the term " bronzes." Its oxides and other compounds are also employed as colouring-agents for ceramic and glass ware, and for combatting fungoid and other plant pests.

Copper is hardened by working, and can be annealed by heating to about 700° C. The rate of cooling has no effect on its hardness. It is crystalline, but not markedly so unless very carefully annealed (see Fig. 66, electrolytic copper, melted, rolled, and annealed.)

Brass consists of copper and zinc. The two metals may be melted together in almost any proportion without actual separation taking place on solidification. Whether brass is a chemical compound or simply a solid solution of the one in the other need not here be discussed. The composition of the ordinary material may be expressed by the formula Cu_2Zn, but much of the brass in use contains nearly 70 per cent. Cu and 30 per cent. Zn, whilst the above formula requires 66 of Cu and 34 Zn.

Zinc (which see) is highly crystalline and brittle. Brass is harder than copper, more malleable than zinc, and not so coarsely crystalline, When melted and cast in chill brass shows a peculiar structure, but no crystals on an etched surface (see Fig. 67).

On annealing at 800° C. for six hours a crystalline structure is developed (see Fig. 68).

Brass after severe working also shows no crystals, but a confused structure (see Fig. 69), head of cartridge case, portions of which show the flowing of the metal, under pressure, and dislocation of the regular structure), and becomes very hard. After this stage continued working may produce fracture. When this hard brass is annealed at 950° C. a large crystalline structure is developed (see Fig. 70).

A temperature of about 750–800° C. seems the most suitable. The structure produced is not so coarsely crystalline, and (from experiments) it may be "worked" to a greater extent after annealing at this temperature than at any other.

BRONZES were originally alloys of copper and tin only. Melted tin dissolves copper somewhat rapidly, and the two may be mixed in almost any proportion whilst liquid, but with some separation on cooling. Several definite compounds are formed. The colour and hardness of copper are much affected by comparatively small amounts of tin.
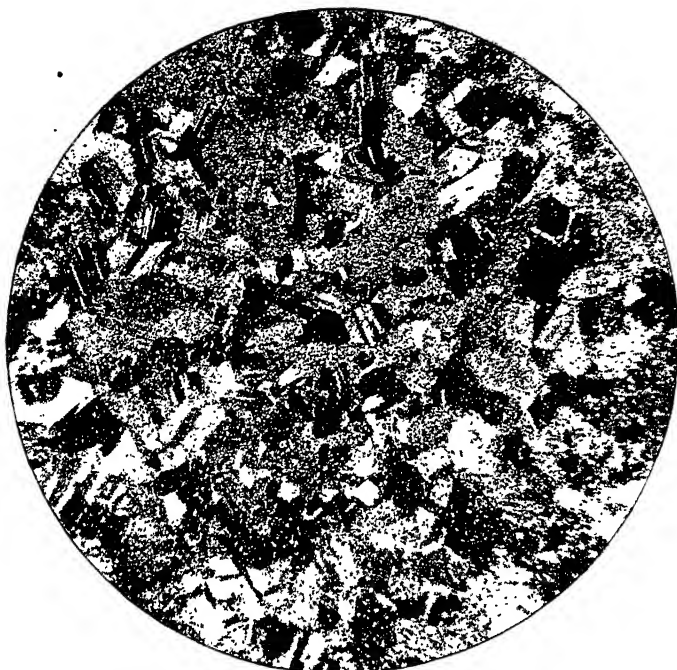
FIG. 66.—Electrolytic copper, rolled and annealed. (× 70.)

FIG. 67.—Brass cast in chill (70 per cent. Cu, 30 per cent. Zn). (× 75.)

Many alloys of copper are now called bronzes, although they contain no tin.   Aluminium bronze, for instance, consists, generally, of 10 per cent. aluminium and 90 per cent. copper.

Copper has the power of dissolving, if not of combining with, many metals, non-metals, and even compounds of other metals, such as the phosphides of nickel, chromium, cobalt, &c., and with arsenic and antimony compounds.   Cuprous oxide is also soluble in the metal.

Many of the bronzes can be cast, become hard on working, and can be annealed by heating to definite temperatures.   They do not, as a rule, harden on chilling.

Gun metal contains from 9 to 10 per cent. tin.   Bell metals are somewhat similar, but often contain small quantities of other metals in addition to tin.   Phosphor-bronze contains about 2 per cent. tin and traces of phosphorus; coinage bronze about 4 per cent. tin and smaller quantities of other metals.   Manganese and other bronzes contain very frequently zinc as well as tin, and in some cases tin is absent. German silver is really a brass containing about 15 per cent. nickel (see " Zinc ").

When the proportion of tin in real bronze exceeds 10 per cent. the alloy becomes too hard and brittle to be worked.   It also whitens, and with 30 per cent. and more of tin is quite white and exceedingly hard, but brittle.   These alloys rich in tin are sometimes called speculum metals.   They take a fine polish, and generally the surface resists the atmosphere well.

The copper alloys most largely employed after brass are various tin-containing bronzes, cupro-nickel, and manganese and aluminium bronzes.   The gold and silver coinage of most nations contains also copper.   It has the effect of hardening gold and silver, when present in small amount, without serious detriment to the natural colour of these metals.

Experiments with Copper.

I. Heated in air, a clean metallic surface changes through many colours, finally becoming black.   A black crust detaches; this is CuO, which does not melt or change on further heating.

The red oxide, Cu_2O, adheres to the metal.

A wire easily melts in the Bunsen flame.

II. With sulphur in tube it combines readily, forming a bluish black mass which melts and is crystalline. It is generally a mixture of the two sulphides.

III. Hydrochloric acid has but little action on a clean surface of metallic copper in the absence of oxygen.

Strong sulphuric dissolves the metal when boiled on it, SO_2 gas escaping. $CuSO_4$ is formed. $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$.

Nitric dissolves it rapidly, oxides of nitrogen being at the same time formed.   The greenish blue liquid on evaporation gives crystals of copper nitrate, $Cu2(NO_3)$, which are very soluble in water.

Organic acids act only with the aid of air or on oxidised surfaces.

The oxides dissolve quickly in acids. They also dissolve in ammonium hydroxide, giving either a colourless (cuprous) or a deep blue solution (cupric).

IV. Metallic copper is acted upon by ammonium hydroxide, assisted by air or *any oxidising substance*, or salts of halogens. The same blue compound, CuN_2H_4, as from the oxide is formed. Most alkaline substances also corrode the metal when air and moisture are present, a green basic carbonate being formed.

Solutions of chlorides or nitrates, in presence of air, also corrode the metal somewhat rapidly. Melted ammonium nitrate dissolves copper with considerable rapidity, and the action may become quite explosive in character.

Unless the copper surface be absolutely clean, an action is also observable in a few minutes on warming with many organic compounds even when air and water are absent.

Dry Reactions.

Copper minerals are very numerous; and as many of them exhibit precisely similar blowpipe reactions, a knowledge of their physical character is indispensable to enable the student to distinguish them readily. Wet tests are, perhaps, the most delicate for copper.

The most characteristic dry reaction is that which copper compounds give when heated in a bead of borax or microcosmic salt before the blowpipe flame. The bead is green whilst hot, blue on cooling. Most copper compounds, when heated on platinum wire in the inner flame, impart an intense green colour to the outer flame. A very minute quantity of copper can be detected by the spectroscope, or by mixing a small quantity of the mineral with sal ammoniac and heating on platinum foil in a colourless flame (see, conversely, "Halogens," later).

All copper compounds are reduced when heated in the inner flame on charcoal, together with sodium carbonate and potassium cyanide, yielding red metallic scales or globules. Sulphides give off SO_2, when roasted in an open tube, and leave CuO behind. Malachite or azurite gives off water and carbon dioxide when gently heated in a tube. Blue vitriol loses water, sulphur dioxide and oxygen, and leaves cupric oxide. Cupric phosphate, arsenate, and silicate fuse to coloured glasses.

Cupric Salts: Examination in Solution.

Hydrochloric acid in the presence of air dissolves copper slightly, forming a little Cu_2Cl_2. Nitric acid is the most active solvent, forming cupric nitrate. Sulphuric acid (concentrated and hot) dissolves the metal.

The sulphate, nitrate, and chloride are soluble in water.

Cuprous salts are mostly insoluble.

SH_2 (group reagent) gives a brownish black precipitate of cupric sulphide (hydrated), CuS, insoluble in dilute acids; slightly soluble in yellow ammonium sulphide; soluble with decomposition in nitric

acid ; completely soluble in potassium cyanide ; insoluble in potassium and sodium sulphides or alkali hydroxides.   CuS is easily oxidised to the sulphate on exposure to air.

$(NH_4)_2S$ produces the same precipitate, somewhat soluble in excess, especially in yellow ammonium sulphide.

NaHO or KHO gives a light blue precipitate of $Cu(HO)_2$.   The precipitate turns black when the solution is heated, and becomes denser, losing some water of hydration.   Three molecules of $Cu(HO)_2$ lose two molecules of OH_2 and leave $3(CuO),OH_2$.   In the presence of many organic substances, such as grape sugar, tartaric, and a number of organic acids, especially di- and tri-basic acids and substances of the nature of urea, N_2H_4CO, the precipitate dissolves to a deep blue solution, whence the whole of the copper is reprecipitated on boiling in the form of bright red cuprous oxide, Cu_2O.

Na_2CO_3, or K_2CO_3, produces a greenish blue basic carbonate, of the composition $CuCO_3,Cu(OH)_2$, carbon dioxide being evolved.   This precipitate is converted on boiling into the black precipitate of $3(CuO),OH_2$.   It is soluble in ammonium hydroxide to an azure blue, and in potassium cyanide to a colourless fluid containing a soluble double cyanide, $Cu(CN)_2 2KCN$.*

Hydroxylamine or hydrazine salts in an alkaline solution reduce all copper salts first to cuprous oxide and then to metal.

Ammonium hydroxide, or its carbonates, when added in small quantities, produces a greenish blue precipitate of a basic salt, which dissolves readily in excess of the reagents, and forms a magnificent azure-blue liquid—a blue which is perceptible if a solution contains only minute traces of copper.   The blue colour is due to the formation of some cupramine compound, whence the black copper oxide separates on boiling with sodium hydroxide, and ammonia escapes.

KCy gives a greenish yellow precipitate of cupric cyanide, $CuCy_2$, soluble in excess. SH_2 produces no precipitate from this solution.

K_4FeCy_6 gives a reddish brown precipitate of cupric ferrocyanide, Cu_2FeCy_6, insoluble in dilute acids, decomposed by potassium or sodium hydroxide with separation of $3CuO,OH_2$.   Even in extremely dilute solutions of copper salts a brownish colour is produced—best seen by looking through a long layer of the solution.

Metallic zinc, iron, aluminium, or magnesium precipitate metallic copper, especially in the presence of a little free hydrochloric acid. If a few drops of a slightly acidulated dilute copper solution are placed on platinum foil (the lid of a platinum crucible), together with a small piece of sheet zinc, the platinum becomes rapidly coated with a reddish film of metallic copper, visible even in the case

* K
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 N : C
  /   \
N : C — Cu — C : N
  \   /
   C : N
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    K.
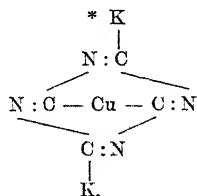
of very dilute solutions, an equivalent quantity of zinc being dissolved.

Ammonia in aqueous solution is rapidly oxidised by copper oxide, with the formation of cupramine, CuN_2H_4, in solution, nd possibly hydrated. The same substance is formed by the combined action of air and ammonium hydroxide on copper, and this solution is largely used in the manufacture of so-called Willesden fabrics and to gelatinise cellulose as a preliminary to forming the threads or filaments of carbon incandescence electric lamps, artificial silk, &c.

CUPROUS SALTS.—Copper resembles mercury in existing in combination in two forms ; or exhibiting two degrees of extent of combination energy with other elements, expressed by the terms cuprous and cupric. For instance, it combines with oxygen to form an oxide, CuO, and another one of half the oxygen content, Cu_2O, and similarly with sulphur, CuS and Cu_2S, and with the halogens ($CuCl_2$ and Cu_2Cl_2), &c.

Some of the chemical energy of the copper atom is doubtless expended on itself or latent in cuprous compounds, e.g., $Cu_2O =$ Cu—Cu.

$$\diagdown O \diagup$$

Cuprous oxide, when treated with concentrated hydrochloric acid, forms cuprous chloride, Cu_2Cl_2, which is colourless when pure. Other acids decompose it into metallic copper and cupric oxide, which latter dissolves in the acid as a cupric salt. Cuprous chloride, when moist or in solution, absorbs oxygen readily and is a powerful reducing agent. It combines with CO, and is used in gas analysis for this reason.

Acetylene, C_2H_2, ethylene, C_2H_4, and other unsaturated hydrocarbons, combine with cuprous compounds, forming a red-coloured cuprous acetylide, &c. These are more easily formed from ammoniacal than from acid solutions. They are very insoluble in water and are explosive when dry.

Cupric salts treated with SO_2 and C_2H_2 also give the acetylide.

Cuprous Compounds.—To a solution of cuprous chloride, Cu_2Cl_2, in concentrated hydrochloric * acid add—

OH_2 ; a white precipitate of Cu_2Cl_2 is produced, because the compound is dissociated and Cu_2Cl_2 is not soluble in water or dilute acid.

KHO gives a yellow precipitate of $Cu_2(HO)_2$, insoluble in excess; it attracts oxygen very rapidly, being converted into cupric hydroxide.

KI, in the presence of sulphurous acid or ferrous sulphate, precipitates from cupric salts greenish-white cuprous iodide, Cu_2I_2, soluble in excess of the iodide.† Both sulphurous acid and ferrous

* This solution in HCl is undoubtedly a compound, $Cu_2Cl_2 2HCl$.
† This is another so-called double salt, K—I———I

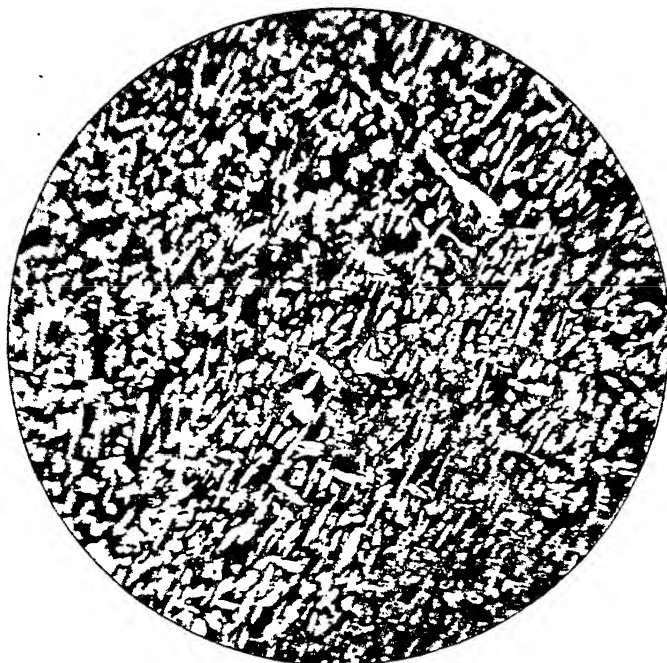$$\left| \begin{array}{c} Cu \diagup \\ | \\ Cu \\ \diagup \end{array} \right|$$

I———I—K.
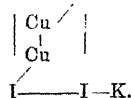
FIG. 71.—Manganese brōnze, cast in sand. (× 70.)

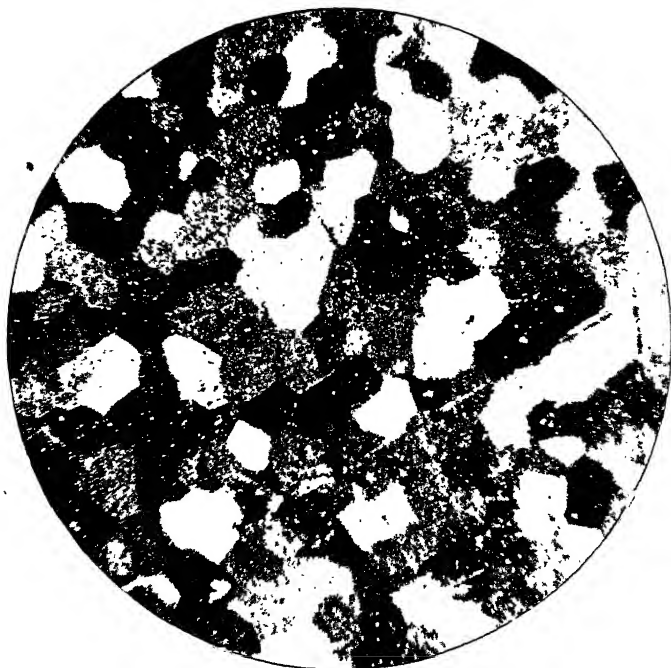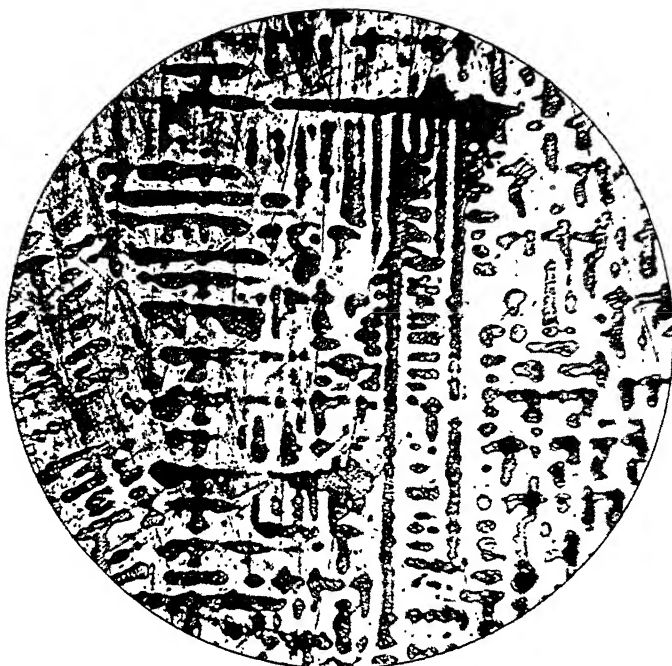FIG. 72.—Manganese bronze, cast in chill. (× 70.)

FIG. 73.—Gun metal (9 per cent. tin), cast in chill, polished, and etched. (× 70.)

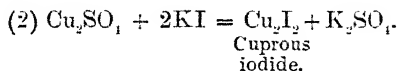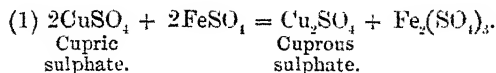FIG. 74.—The same gun metal, forged into bar and then annealed at 800° C. (× 70.)

FIG. 77. — Halfpenny bronze 4·2 per cent. Sn.   (× 70.)

sulphate are reducing agents, which, by the absorption of oxygen from the cupric salts, are converted into H_2SO_4 and $Fe_2(SO_4)_3$, thus:

$$(1)\ 2CuSO_4 + 2FeSO_4 = Cu_2SO_4 + Fe_2(SO_4)_3.$$
Cupric sulphate.   Cuprous sulphate.

$$(2)\ Cu_2SO_4 + 2KI = Cu_2I_2 + K_2SO_4.$$
Cuprous iodide.

NH_4SCy and a reducing agent, as SO_2, form white cuprous sulphocyanate, $Cu_2(SCy)_2$, insoluble in water, and not affected by dilute acids excepting nitric. In the presence of H_2SO_3 this precipitate is very insoluble, and gives a good method of separation of copper from many other metals.

(5) **CADMIUM,** Cd''.—Cadmium occurs in nature along with zinc minerals and resembles that metal to some extent both in chemical and physical properties.

Greenockite, CdS, is the only well-marked cadmium mineral, but most zinc ores contain a small amount. It is not so coarsely crystalline as zinc, nor is the blue tint so well marked.

Atomic weight = 111·84. Relative weight = 8·60. It melts at 315° C. and boils at 770°C. It can therefore be distilled, and is, in fact, generally obtained from the early portions of the zinc distillate in the process of extraction of that metal. Cadmium vapour burns with a brown flame or smoke of CdO. It does not rapidly rust in water, but tarnishes in air at about the same rate as zinc.

It is very malleable at the ordinary temperature. (Difference from zinc.) The common acids easily dissolve the metal, and alkalies act upon it, but less rapidly than on zinc. It dissolves quietly in ammonium nitrate solution with scarcely any gas evolution. In the fused state ammonium nitrate dissolves the metal rapidly, and the final product may " puff off " or almost explode if strongly heated. Cadmium enters into the composition of a few alloys where " fusibility " is desired. Most metals seem capable of uniting with it, but owing to its low melting-point and its volatility it tends either to separate or pass off in vapour if the other metal has a high melting-point. It is less electro-positive than zinc.

Experiments.

I. Heated in tube in air, shows colours finally passing into brown ash or oxide, CdO, which does not melt or volatilise, but generally a little metal will volatilise and form a dark brown sublimate or mirror in the tube. The oxide formed on the surface on gently heating, below melting, adheres closely to the metal.

II. Sulphur does not unite *very* easily with cadmium when heated in the tube, but more easily than with zinc.

On heating to the vapourising temperature of the metal, combina-

13

tion takes place very energetically, a beautiful yellow sulphide, CdS, being formed; it is rosy red when hot.

III. Dilute warm hydrochloric, sulphuric, and nitric acids dissolve the metal and form colourless crystalline compounds. The acids when cold and dilute act but slowly.

The oxide dissolves readily in the three acids. Ammonium hydroxide also dissolves the oxide, but not very rapidly after it has been heated strongly.

IV. Alkalies also dissolve the metal, but not so rapidly as is the case with zinc.

Dry Reactions.

Cadmium compounds, when mixed with sodium carbonate and heated on charcoal in the inner blowpipe flame, give a characteristic brown incrustation—*i.e.*, they are readily reduced to the metallic state; but the metal being highly volatile, is reoxidised on its passage through the outer flame. Cadmium is recognised with more difficulty when it is in combination with zinc—as, for instance, in cadmiferous blende. By heating, however, a mixture of blende and sodium carbonate and potasssum cyanide for a few moments only on charcoal or in a tube a slight brown incrustation is generally obtainable before the zinc is volatilised. Cadmium oxide turns the bead of borax or microcosmic salt yellowish whilst hot, colourless when cold, but this is of no use as a test when other substances are present.

Reactions in Solution.

Most ordinarily occurring cadmium compounds, as sulphate, chloride, iodide, nitrate, acetate, &c., are soluble in water, and all others are soluble in acids. They are mostly colourless.

SH_2 (group reagent) gives from dilute solutions a fine yellow precipitate of cadmium sulphide, CdS, used as a permanent yellow paint, insoluble in alkali sulphides, hydroxides, or cyanides; insoluble in cold, but soluble in hot, dilute nitric and hydrochloric acids; soluble also in dilute sulphuric acid. (Distinction from copper.)

Hence the separation of cadmium by means of SH_2, especially from acid solutions, is frequently left either incomplete, or is not effected at all, in Group II., unless the precaution be taken of nearly neutralising the free acid with ammonia, before passing SH_2, as well as neutralising the mineral acid as fast as it is liberated by the SH_2.

$(NH_4)_2S$, same precipitate.

KHO, a white precipitate of $Cd(HO)_2$, insoluble in excess.

NH_4OH, same precipitate, soluble in excess.

Alkali carbonate free from caustic alkali gives a white precipitate of cadmium carbonate, $CdCO_3$, insoluble in excess.

KCy gives a white precipitate of cadmium cyanide, $CdCy_2$,* soluble in excess. Sulphuretted hydrogen precipitates CdS from this solution. (Distinction from copper.)

* See double cyanides.

Metallic zinc precipitates cadmium from its solutions as a crystalline powder, which assumes metallic lustre on rubbing with a hard substance.

Separation of the metals of Subdivision A, Group II.—viz., mercury, lead, bismuth, copper, cadmium, whose sulphides are insoluble in ammonium sulphide or sodium hydroxide.

The precipitate produced by the group reagent SH_2, which is insoluble in ammonium sulphide or sodium hydroxide, may consist of all the five sulphides, or only of one, two, &c. A precipitate of a bright yellow colour, e.g., would be indicative of cadmium sulphide only. If the precipitate is black, it is necessary to examine for all the five metals.

It has already been seen that the sulphides of the metals of this subdivision are—

1st. Insoluble in alkalies and alkali sulphides, and

2nd. Insoluble in dilute acids, or nearly so, but soluble in concentrated acids.

Concentrated nitric acid (free from chlorine), diluted with its own bulk of water, dissolves four out of the five sulphides—viz., PbS, Bi_2S_3, CuS, and CdS—with separation of sulphur,[*] mercuric sulphide being completely soluble only in aqua regia. Hence by boiling with dilute nitric acid (in the absence of HCl) mercury may be separated from the other metals of Subdivision A. Concentrated nitric acid converts PbS partially into $PbSO_4$, by the simultaneous oxidation of the sulphur. HgS would be, therefore, found in the residue, as well as $PbSO_4$ and S. But the whole of the PbS can be converted into sulphate only by boiling with fuming nitric acid, and as lead sulphate is slightly soluble in concentrated nitric acid the lead would not be entirely removed as sulphate. This difficulty is overcome by boiling the whole of the sulphides with dilute nitric acid, as mentioned, then diluting with water and adding dilute sulphuric acid, and, lastly, when cold, adding to the solution its own bulk of alcohol (methylated spirit). If a residue is left it may be white, indicative of the presence of $PbSO_4$, or black, from the presence of HgS. Sulphur may also be left. The solution contains the metals Bi, Cu, Cd.

Examination of the Residue.—Lead sulphate dissolves readily in certain salts, such as ammonium acetate or tartrate, also in strong HCl when hot. By treating the residue, therefore, with a concentrated solution of ammonium acetate, the $PbSO_4$ is dissolved out. The absence of mercury compounds may be inferred if no black, but only a yellow, residue of sulphur is left, and if no mercury has been indicated by the reactions in the dry way. The presence of both lead and mercury should, however, invariably be confirmed by special tests—viz., the lead by means of potassium chromate, and the mercury by heating the dry residue in a bulb tube with dry sodium carbonate.

Examination of the Solution.—It has been seen that NH_4OH precipitates $Bi(HO)_3$, which is insoluble in excess, whilst $Cu(HO)_2$

[*] A little H_2SO_4 is also formed.

and $Cd(HO_2)$ are likewise precipitated, but are soluble in excess. If a white precipitate be obtained on adding NH_4OH, the inference is that bismuth is present. (Should the lead not have been removed entirely, some $Pb(HO)_2$ would be also precipitated.) The precipitate is filtered off and well washed, then redissolved in a little hydrochloric acid, and precipitated by the addition of much water.* The ammoniacal filtrate is of a fine azure-blue colour when copper—even in small quantities—is present. If colourless, and if, by the addition of SH_2, a fine yellow precipitate comes down, the inference is that no copper is present, but only cadmium. If a black precipitate comes down on passing the gas through the slightly acidulated (HCl) solution, the presence of copper and possibly of cadmium is indicated. These two metals can be separated either by means of KCy (CdS being insoluble in potassium cyanide) or dilute sulphuric acid (CuS being insoluble in hot dilute sulphuric acid). Filter again; in the one case copper is left in solution, in the other cadmium. It is not difficult to identify these two metals by special tests.

The separation of the metals mercury, lead, bismuth, copper, and cadmium is therefore based upon—

1st. The insolubility of HgS in nitric acid.

2nd. The formation of $PbSO_4$, and its solubility in ammonium acetate.

3rd. The insolubility of $Bi(HO)_3$ in excess of ammonium hydroxide.

4th. The insolubility of CuS in dilute sulphuric acid, or its solubility in potassium cyanide.

A tabular scheme for their separation is given in the Analytical Tables, Table II.

GROUP II. SUBDIVISION B.

(1) **TIN**, Sn″ and [iv].—This metal is found in nature mainly in the form of tinstone or cassiterite, SnO_2, sometimes combined with sulphur, as tin pyrites, SnS_2, (bell-metal ore). The metal is obtained by the reduction of its oxide, SnO_2, by carbon at a high temperature. It is white, with a slight yellow tint. Atomic weight $=117.70$; relative weight, 7.29; melting-point, $230.9°$ C.; boils between $1450°$ and $1600°$ C. Soft, but does not mark paper like lead. Tin, although very malleable, is a very crystalline metal, as may be noticed when a piece is treated with a dilute acid—crystalline markings appear; also on bending a creaking or "scream" is noticed, due, doubtless, to the rupture of contact between crystal faces. This element is related to carbon (see Newland's table, *ante*).

Tin is much used alone in the form of tinfoil, and also in many alloys. Tin "ware" is iron coated with tin—a superficial alloy only. Copper is "tinned" for protection against chemical actions. Some bronzes contain tin (see "Copper"). Pewter should be tin with 1 or 2 per cent. only of lead.

* Much water here means pouring the 3 or 5 c.c. of solution into about 500 c.c. of water.

Fig. 79.—Tin, lead, antimony, rapidly cooled after fusion (Sn 45, Pb 40, Sb 15 per cent.). (× 70.)

Fig. 80.—Tin, lead, antimony, slowly cooled after fusion. (× 70.)

Solder consists of tin and lead. "White metals" contain tin, lead, antimony, and sometimes copper. The micrographs shown by Figs. 79 and 80 are of an alloy of tin, lead, and antimony. It is white, and takes a good polish.

The metal does not oxidise in air, excepting when heated to its melting-point. Water has no action at ordinary temperatures, and dilute acids and alkalis little, if any. Concentrated HCl dissolves it when heated or when in presence of platinum.* Strong nitric acid converts it into metastannic acid. Fused alkalies also act on the metal at a high temperature, oxidising it, and then combining with the oxide, forming stannates. It exhibits two, if not three, stages or degrees of energy in its combinations with other substances. For instance, oxides, SnO, Sn_2O_3, SnO_2 ; chlorides, $SnCl_2$, $SnCl_4$.

Tin dissolves slowly in hot hydrochloric acid ; readily in aqua regia, with formation of $SnCl_4$. Nitric acid converts tin into metastannic acid, $Sn_5O_5(HO)_{10}$, which by evaporation and ignition is converted into SnO_2. Tin forms very few real salts. Its metallic or basic nature is but slight. It is, in fact, a member of the carbon group, and shows a greater tendency to form acid than basic compounds. All the members of this group form an oxide, MO_2, which exhibits acid characters.

Experiments.

I. Heated in a tube in air : after melting, coloured films pass over surface of globule. A grey ash forms, which does not melt, but becomes yellow-brown when hot, pale yellow when cold. It is SnO_2.

II. With sulphur combination takes place readily, with heat evolution. The product is blackish, soft, fusible, and crystalline, $=SnS$.

III. Hot hydrochloric dissolves tin ; hydrogen escapes, $SnCl_2$ is formed. On evaporating in dish white crystals may be obtained. A large quantity of water added to the crystals will produce a white amorphous hydrated compound, owing to hydrolysis.

Sulphuric has little or no action unless boiling, and then only slowly, with evolution of SO_2.

Nitric acid acts violently ; red gases escape and a white powder is formed, which does not dissolve either in the acid or in water. Strong HCl slowly dissolves this powder. Oxide of tin prepared as in I. is almost insoluble in all acids. Strong NaHO dissolves it to some extent.

IV. Ammonia is without action on the metal or oxide. KHO and NaHO in very concentrated solution act on the metal, hydrogen being slowly evolved. The presence of another metal, as iron or platinum, assists this solution in alkalies by forming a galvanic couple.

Melted ammonium nitrate also oxidises the metal to SnO_2.

* It may be remarked that it is extremely likely that a perfectly pure metal, even one ordinarily considered positive in chemical character, would be unacted upon by acids, the small amount of impurity in ordinary metals sufficing to set up a voltaic action, under the influence of which they are attacked more easily.

Dry Reactions.

When tin minerals are fused on charcoal, with sodium carbonate and potassium cyanide, in a strongly reducing flame, they yield small globules of tin which are malleable, and the charcoal becomes covered with a white coating of SnO_2. If this white incrustation be treated with a solution of cobalt nitrate, and strongly heated, it assumes a bluish green colour, which is characteristic of tin, but is not to be trusted to when other metallic oxides are present. Insoluble stannic oxide, SnO_2, or the native oxide, may also be fused with KHO in a silver crucible, and thus converted into potassium stannate, soluble in water; or it may be rendered soluble by fusion on charcoal with 3 parts of sodium carbonate and 3 of sulphur, when sodium sulphostannate is formed, which is soluble in water, but is decomposed and precipitated as SnS_2 by means of hydrochloric acid.

By introducing into a borax bead—in which sufficient cupric oxide has been diffused to render the bead faintly blue—traces of a stannous compound and heating it in the reducing flame, the bead turns reddish brown or forms a ruby-red glass, owing to the reduction of the copper compound to red cuprous oxide.

Tinstone being insoluble in acids, must be fused with alkali carbonates and a reducing agent, such as potassium cyanide, charcoal, or black flux (ignited Rochelle salt), when metallic tin is obtained.

Tin is capable of forming two series of salts, of oxides, sulphides, &c., viz.:

Stannous compounds.		*Stannic compounds.*		
$SnCl_2$	Stannous chloride.	$Sn^{iv}Cl_4$	Stannic chloride.	
SnO	,, oxide.	$Sn^{iv}O_2$	,,	oxide (anhydride).
$SnSO_4$	,, sulphate.	$Sn^{iv}S_2$	,,	sulphide.
SnS	,, sulphide.			

Stannic acid, H_2SnO_3, combines not only with the strong alkali bases, OK_2, ONa_2, but even with stannous oxide, SnO, to form stannates, *e.g.*, K_2SnO_3, dipotassium stannate; $SnSnO_3$, stannous stannate.

Reactions in Solution.

A. *Stannous Compounds.*—A solution of stannous chloride, $SnCl_2$, is employed.

SH_2 (group reagent) gives a dark brown precipitate of stannous sulphide, SnS, insoluble in ammonium hydroxide; nearly insoluble in normal ammonium sulphide, but readily dissolved in the presence of sulphur or by the yellow sulphide; from this latter solution it is reprecipitated as yellow stannic sulphide, SnS_2, on the addition of hydrochloric acid. It is also soluble in potassium or sodium hydroxides, from which hydrochloric acid precipitates SnS unchanged. Soluble in boiling hydrochloric acid.

$(NH_4)_2S$ gives the same precipitate. Soluble in large excess.

KHO or NaHO gives a white bulky precipitate of $2(SnO),OH_2$, soluble in excess to potassium stannite, K_2SnO_2.

Ammonium hydroxide or carbonate, same precipitate, insoluble in excess.

By far the most interesting reactions are based, however, upon the tendency of stannous salts to become converted into stannic salts. $SnCl_2$ combines directly with two more atoms of chlorine to become $SnCl_4$, whereby the chemical affinities of tin for chlorine become satisfied. Stannous compounds may be viewed as unsatisfied bodies, which can deprive certain other bodies of chlorine, oxygen, &c.

$HgCl_2$ added to a solution of $SnCl_2$ produces first a white precipitate of mercurous chloride, Hg_2Cl_2, and when boiled with excess of $SnCl_2$ a greyish powder of metallic mercury.

$CuCl_2$ is reduced by $SnCl_2$ to cuprous chloride, Cu_2Cl_2, with formation of $SnCl_4$.

Fe_2Cl_6 yields two atoms of chlorine to $SnCl_2$, forming $SnCl_4$, and leaving two molecules of $FeCl_2$. The yellowish solution turns green or colourless.

Potassium permanganate or dichromate solutions, in the presence of an acid, become colourless and green respectively when $SnCl_2$ is added to them.

$AuCl_3$ gives with $SnCl_2$ a purple precipitate (purple of Cassius), which may be viewed as $Au_2 + 3SnO_2$. The change may be expressed thus : $2AuCl_3 + 3SnCl_2 + 6OH_2 = Au_2 + 3SnO_2 + 12HCl$.

This is a most delicate reaction, especially when the $SnCl_2$ contains a little $SnCl_4$.

B. *Stannic Compounds.*—A solution of stannic chloride, $SnCl_4$, or bromide, $SnBr_4$, is almost the only form in which it can be employed for these tests. These compounds are decomposed by much water, so the solution must be fairly strong and have a slight excess of acid (HCl).

SH_2 (group reagent) gives a yellow precipitate of stannic sulphide, SnS_2, readily soluble in alkali sulphides, potassium hydroxide, boiling concentrated hydrochloric acid, and aqua regia ; soluble, although somewhat slowly, in ammonium hydroxide (distinction from SnS), and insoluble in ammonium hydrogen carbonate.
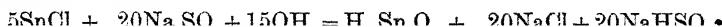
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Soluble carbonates give the same precipitate.

Stannic chloride furnishes an interesting case of precipitation— viz., by means of neutral salts, such as sodium sulphate, ammonium nitrate (in fact, most neutral salts). Metastannic acid, $H_{10}Sn_5O_{15}$, is precipitated on heating, provided the solution of stannic chloride is not too acid, thus :

$5SnCl_4 + 20Na_2SO_4 + 15OH_2 = H_{10}Sn_5O_{15} + 20NaCl + 20NaHSO_4$

Dry Reactions.

When tin minerals are fused on charcoal, with sodium carbonate and potassium cyanide, in a strongly reducing flame, they yield small globules of tin which are malleable, and the charcoal becomes covered with a white coating of SnO_2. If this white incrustation be treated with a solution of cobalt nitrate, and strongly heated, it assumes a bluish green colour, which is characteristic of tin, but is not to be trusted to when other metallic oxides are present. Insoluble stannic oxide, SnO_2, or the native oxide, may also be fused with KHO in a silver crucible, and thus converted into potassium stannate, soluble in water; or it may be rendered soluble by fusion on charcoal with 3 parts of sodium carbonate and 3 of sulphur, when sodium sulphostannate is formed, which is soluble in water, but is decomposed and precipitated as SnS_2 by means of hydrochloric acid.

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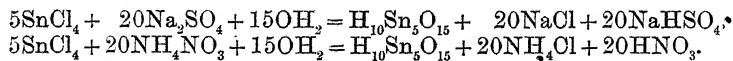
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$$5SnCl_4 + 20Na_2SO_4 + 15OH_2 = H_{10}Sn_5O_{15} + 20NaCl + 20NaHSO_4.$$
$$5SnCl_4 + 20NH_4NO_3 + 15OH_2 = H_{10}Sn_5O_{15} + 20NH_4Cl + 20HNO_3.$$

Metallic zinc precipitates from acid solutions of stannous or stannic chloride metallic tin in the form of grey laminæ, or of a spongy mass which can be readily dissolved in hydrochloric acid, especially when in contact with a piece of platinum foil. Metallic iron produces no precipitate, but reduces to a stannous salt.

Metallic tin reduces stannic to stannous chloride, thus :
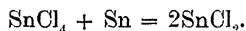
$$SnCl_4 + Sn = 2SnCl_2.$$

Copper similarly : $2Cu + SnCl_4 = SnCl_2 + Cu_2Cl_2.$

A solution of stannous chloride (containing hydrochloric acid) cannot be kept, when exposed to air, without changing to stannic chloride and insoluble stannous oxychloride, Sn_2OCl_2, on account of the great attraction which stannous salts possess for oxygen, thus :

$$(1)\ 2SnCl_2 + O = Sn_2OCl_2 + Cl_2.$$
$$(2)\ SnCl_2\ \ +Cl_2 = SnCl_4.$$
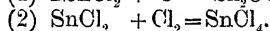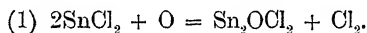
Hence granulated metallic tin or pure tinfoil is usually put into stannous chloride solutions in order to prevent the oxidation, and an excess of free acid to prevent precipitation.

(2) **ANTIMONY,** Sb''' and ^{v}.—Is sometimes found in the metallic state ; also in combination with oxygen as white antimony, Sb_2O_3, but more frequently as sulphide, Sb_2S_3 (grey antimony, stibnite), and in combination with other metallic sulphides (Ag_2S, PbS, Cu_2S), as sulphantimonite and sulphantimonate.

Metallic antimony is eminently crystalline, brittle, and of a bluish grey colour. Atomic weight $= 119\cdot6$; relative weight, $6\cdot71$. Melts at 440° C., and boils between 1090° and 1450° C.

It combines with many metals, forming distinct compounds, most of which are hard, crystalline, and brittle. Type metal contains about 15 per cent., and other lead alloys smaller amounts. Where ductility or malleability is desired antimony must be absent. Its presence is therefore in many cases objectionable—as, for instance, in copper or brass. It is the " hardening " element in some alloys of lead and tin. When heated it gives off vapour below the temperature above given as the boiling-point.

Water and acids, with the exception of nitric, have little or no action at ordinary temperatures. It combines with oxygen, sulphur, and the halogens directly, and with considerable energy, in two degrees, forming two distinct classes of compounds.

Antimonious compounds.		*Antimonic compounds.*	
$SbCl_3$	Antimonious chloride.	$SbCl_5$	Antimonic chloride.
Sb_2O_3	„ oxide.	Sb_2O_5	„ oxide.
Sb_2S_3	„ sulphide.	Sb_2S_5	„ sulphide.
$HSbO_2$	Metantimonious acid.	$HSbO_3$	Metantimonic acid.

Both these acids can enter into combination with strong bases, such as the alkalies, to form weak salts—metantimonites and metantimonates, viz. :

KSbO$_2$, Potassium metantimonite.
KSbO$_3$, Potassium metantimonate.
NaSbO$_3$, Sodium metantimonate.

Sb$_2$O$_4$ is formed when antimonic oxide (obtained by the action of nitric acid upon antimony) is ignited. This compound is of some importance, as it serves for the quantitative estimation of antimony.

Experiments.

I. Heated in air, the metal melts readily and begins to give off white vapours, which condense on cooler parts of tube. A white crystalline oxide forms on and surrounds the globule of melted metal. It is Sb$_2$O$_3$, which fuses to a yellow mass and begins to sublime at a red heat.

II. Heated with sulphur, combination easily takes place, some of the product *subliming* to the upper part of the tube by the heat evolved. The product is a reddish black, especially the sublimate.

III. Hydrochloric acid has no action on the metal. Sulphuric, even when concentrated and hot, has only a very slow action.

Nitric oxidises the metal to a white amorphous powder containing Sb$_2$O$_3$ and Sb$_2$O$_5$, which is quite insoluble in nitric acid, but dissolves in some other acids and in alkaline solutions.

Alkali hydroxides dissolve both the oxide produced as in I., or the sulphides as in II. The metal is unaffected by alkalies or ammonia.

N.B.—If the melted globule obtained in I. be thrown out on to a large piece of paper it will break up, and the small globules will glow brightly and flow over the paper, leaving white *and* brown lines or streaks, partly oxide, partly metal, showing that both metal and oxide were in vapour.

Dry Reactions.

On heating metallic antimony or an antimony mineral—*e.g.*, grey antimony—with free access of air, either on charcoal or in a glass tube open at both ends, dense white fumes of antimonious and antimonic oxides are given off, which condense on the colder part of the charcoal or glass tube, thus : Sb$_2$S$_3$ + 9O = Sb$_2$O$_3$ + 3SO$_2$.

All compounds of antimony can be reduced to the metallic state when heated on charcoal with sodium carbonate and potassium cyanide. A brittle globule of metallic antimony is obtained, giving off dense white fumes of Sb$_2$O$_3$ (even after the withdrawal of the metal from the flame), which thickly encrust the metallic globule with a network of brilliant acicular crystals.

This is sometimes difficult to bring about.

Reactions in Solution.

Chlorine and bromine attack antimony violently, forming with it SbCl$_3$ and SbBr$_3$, or SbCl$_5$ and SbBr$_5$, according to the proportions of halogen employed and the temperature at which the combination takes place. Hydrochloric acid has no action upon the metal, but aqua regia dissolves it readily to SbCl$_5$. Nitric acid converts it into

a compound containing Sb_2O_3 and Sb_2O_5, insoluble in nitric acid, soluble in tartaric acid. Grey antimony, Sb_2S_3, as well as Sb_2S_5, dissolves in concentrated hydrochloric acid, with evolution of sulphuretted hydrogen, the latter sulphide with separation of sulphur.

Two distinct classes of compounds exist.

A. *Antimonious Compounds.*—Antimonious chloride dissolved in a little HCl or tartar emetic, potassium antimony tartrate, also in dilute HCl, will give the under-mentioned reactions. There are scarcely any " salts " of antimony.

SH_2 (group reagent) gives an orange-red precipitate of hydrated antimonious sulphide, Sb_2S_3, soluble in alkali sulphides and in potassium or sodium hydroxides; reprecipitated by hydrochloric acid; slightly soluble in ammonium hydroxide; all but insoluble in hydrogen ammonium carbonate and in hydrogen ammonium or hydrogen potassium sulphites. It dissolves in boiling concentrated hydrochloric acid.

Temperature and concentration of the reagents produce reciprocal effects.* In a cold dilute hydrochloric acid solution the $SbCl_3$ exchanges its chlorine for sulphur with SH_2, Sb_2S_3 being precipitated, whilst boiling concentrated hydrochloric acid dissolves Sb_2S_3 readily, with evolution of SH_2.

$(NH_4)_2S$ produces the same precipitate as SH_2, soluble in excess.

KHO or NaHO precipitates antimonious oxide, Sb_2O_3, readily soluble in excess, with formation of potassium antimonite.

NH_4OH, same precipitate, almost insoluble in excess.

Soluble carbonates, the same precipitate. CO_2 is evolved.

OH_2 decomposes $SbCl_3$, forming a white insoluble basic salt, antimonious oxychloride, SbOCl, soluble in tartaric acid. (Distinction from bismuthous oxychloride, BiOCl.) Water, therefore, gives no precipitate with a solution of potassium antimonyl tartrate (tartar emetic) $C_2H_2(OH)_2{CO_2K \atop CO_2SbO}$; and alkalies and alkali carbonates produce a partial precipitation only after some time.

Metallic Zn, Cu, Cd, Fe, Al, Sn, and Pb precipitate the metal in the absence of free nitric acid as a black powder. Some SbH_3 is liable to be formed.

A rather delicate reaction for antimony consists in precipitating the metal from a dilute hydrochloric acid solution on platinum foil or on the lid of a platinum crucible, by means of a small strip of metallic zinc. H and SbH_3 (antimonietted hydrogen) are evolved,

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* These are mostly mass reactions. The student's attention might have been drawn to them sooner. As a rule, perhaps when more is known, without exception, a chemical reaction is a reversible cycle.

$$a \quad M'' \; + _nH_2O = H_2 \; + M''O + n - 1H_2O.$$
$$b \quad M''O + _nH_2 \; = M'' + H_2O + n - 2H.$$
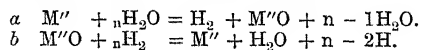
For the completion of each of these equations it requires that n must have a considerable value. These actions may be compared to a crowd of moving molecules succeeding in pushing one or two of their number into some difficult position.

and the platinum is stained brown or black by the deposited metal, (or hydride, Sb_2H_4). Mere traces of antimony can thus be discovered. The stain is little, if at all, affected by hot dilute hydrochloric acid, but disappears on heating with nitric acid. (Tin gives no *black stain* on platinum.) The finely divided metal, as precipitated by zinc, is more readily acted upon by acids than when in a compact state. This is, however, a general property of metals.

Compounds containing triad antimony exhibit a tendency (less marked, however, than in stannous compounds) to combine with more chlorine, &c., and to pass into antimonic compounds.

The following are some of the reactions naturally arising from this tendency of antimonious compounds:

When a current of chlorine gas is passed over solid $SbCl_3$, chlorine is absorbed; the trichloride liquefies, forming pentachloride:

$$SbCl_3 + Cl_2 = SbCl_5.$$
Solid   Liquid
antimonious   antimonic
chloride.   chloride.
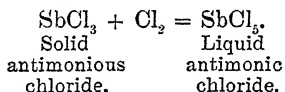
Sodium metantimonite, $NaSbO_2$, is oxidised in the presence of sodium hydroxide by free iodine, with formation of sodium metantimonate, $NaSbO_3$ and NaI, thus:

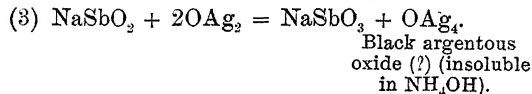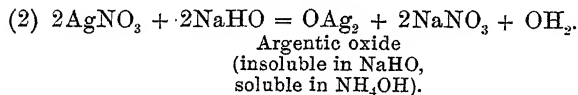$$NaSbO_2 + I_2 + 2NaHO = NaSbO_3 + 2NaI + OH.$$
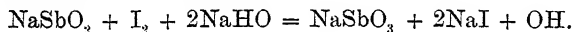
A hydrochloric acid solution of $SbCl_3$ reduces $AuCl_3$ to metallic gold (frequently with separation of $HSbO_3$), thus:

$$3SbCl_3 + 2AuCl_3 = 3SbCl_5 + Au_2.$$
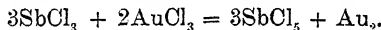
Sodium metantimonite is oxidised in an alkaline solution by argentic oxide, OAg_2, to sodium metantimonate, a lower oxide of silver or perhaps metallic silver [*] being formed, which is insoluble in ammonium hydroxide, OAg_2 being readily soluble. (Distinction between Sb_2O_3 and Sb_2O_5.)

The several reactions may be expressed as follows:

(1) $SbCl_3 + 4NaHO = NaSbO_2 + 3NaCl + 2OH_2.$
Sodium
metantimonite.

(2) $2AgNO_3 + 2NaHO = OAg_2 + 2NaNO_3 + OH_2.$
Argentic oxide
(insoluble in NaHO,
soluble in NH_4OH).

(3) $NaSbO_2 + 2OAg_2 = NaSbO_3 + OAg_4.$
Black argentous
oxide (?) (insoluble
in NH_4OH).
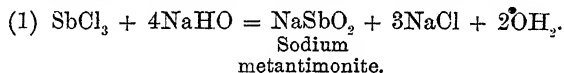
$Na_2S_2O_3$ (sodium thiosulphate) precipitates Sb_2S_3, thus:

$$3Na_2S_2O_3 + Sb_2O_3 = Sb_2S_3 + 3Na_2SO_4.$$
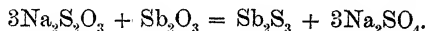
* There is still some question as to the composition of these silver compounds, although a good deal of work has been done on them.

B. *Antimonic Compounds.*—Potassium metantimonate, $KSbO_3$, may conveniently be employed for studying the reactions in an aqueous solution.

This salt is prepared by fusing metantimonic acid, $HSbO_3$, with a large excess of KHO in a silver crucible, or by deflagrating finely powdered metallic antimony with a mixture of potassium nitrate and carbonate in a porcelain crucible, and dissolving the mass in cold water.

$HSbO_3$ fused with NaOH gives sodium metantimonate, which is insoluble in water, or nearly so.

$KSbO_3$ is readily decomposed by concentrated acids (hydrochloric or nitric), metantimonic acid being precipitated. It dissolves in excess of warm dilute HCl.

SH_2 gives from a solution of $HSbO_3$ in excess of hydrochloric acid an orange precipitate of antimonic sulphide, Sb_2S_5, mixed with Sb_2S_3 and S ; soluble in alkali sulphides, readily soluble in ammonium or potassium hydroxides ; also soluble in boiling concentrated hydrochloric acid, with evolution of SH_2 and deposition of S ; only very sparingly soluble in cold hydrogen ammonium carbonate.

$(NH_4)_2S$, same precipitate, soluble in excess.

Ferrous sulphate does not reduce antimonic compounds.

Antimonic compounds, like stannic salts, can, under certain conditions, act as oxidising agents, *e.g.* :

On igniting antimonic anhydride, it splits up into Sb_2O_4 and oxygen.

$SnCl_2$ precipitates $HSbO_2$ from a hydrochloric acid solution of $HSbO_3$, the $SnCl_2$ being converted into $SnCl_4$.

On boiling a solution of $HSbO_3$ in hydrochloric acid, whereby some $SbCl_5$ is produced, with potassium iodide, iodine is liberated, colouring the solution brown. Iodine is set free because $SbCl_5$ on being heated with KI behaves thus: $SbCl_5 + 2KI = 2KCl + I_2 + SbCl_3$. The liberated iodine is readily recognised by means of the starch iodine reaction.* (Distinction between antimonious and antimonic compounds.)

$SbCl_5$ is useful in a number of cases as a " conveyor " of Cl to organic compounds.

(3) **ARSENIC**, As''' and ^{v}.—This element is very widely distributed in small quantities in nature in a state of combination. It is sometimes found native, but exists most frequently united with sulphur as realgar, As_2S_2, and as orpiment, As_2S_3, or arsenious sulphide (sulpharsenious anhydride) ; with metals it exists in arsenical nickel, As_2Ni, copper nickel, As_2Ni_2, and in smaltine, As_2Co. Arsenic acts generally more like a metalloid than a metal. Metallic arsenides are frequently found in combination with metallic sulphides, such as the sulphides of Ag, Fe, Ni, Co, Cu, &c., as in the common mineral mispickel, or arsenical pyrites, $FeAs_2FeS_2$; in nickel glance or grey nickel ore, $NiAs_2,NiS_2$, and in cobalt glance, $CoAs_2,CoS_2$. Arsenic occurs also in

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* See test for iodine with starch paper or starch paste, due to a supposed compound of iodine and starch.

the form of metallic arsenates, such as calcium, magnesium, nickelous, cobaltous, lead arsenates ; for example, in the mineral pharmacolite, $Ca_2As_2O_7,6OH_2$ (calcium pyrarsenate), in nickel ochre, $Ni_3As_2O_8,9OH_2$, in cobalt bloom, $Co_3As_2O_8,8OH_2$, and in mimetesite, $3Pb_3As_2O_8,PbCl_2$, In still smaller quantities or traces it is present in coals, some waters, and many minerals, as iron ores.

Metallic arsenic is highly crystalline, of a dark grey colour, and exceedingly friable. Its atomic weight $= 74\cdot9$; relative weight, $5\cdot73$. It does not melt before volatilising at the ordinary pressure, but under considerable pressure appears to melt at a red heat. It passes into vapour slightly at all temperatures and sublimes in crystals ; distils readily at 449–$450°$ C. It oxidises on exposure to air superficially, and also on contact with water slowly. Acids have no action upon it in the sense of forming salts. Nitric acid oxidises it to arsenic acid. Other substances containing oxygen also attack it. Alkalies dissolve it, hydrogen being liberated. It combines directly with sulphur and the halogens, in addition to oxygen, in two degrees, forming arsenious and arsenic compounds. All these compounds are volatile, mostly without decomposition. It alloys, or unites, with most other metals, and imparts hardness, fusibility, and brittleness, even when in small quantity. This appears to be due to the formation of arsenides, which then dissolve, forming solid solutions (see "Steel," &c.), as is the case with carbides, oxides, sulphides, &c. In addition to the effects above mentioned, the arsenide when contained in this state tends to separate out into veins, &c., to segregate, thus causing dangerously weak places in the metal.

Traces of arsenic are almost invariably found in commercial S, Fe, Cu, Zn, Sn, H, H_2SO_4, and HCl. On account of the solubility of its oxides, arsenic is found in some mineral waters and in the deposits from them.

Arsenic, as element, is scarcely employed ; one or two alloys—shot, for instance—contain it. Its compounds both with oxygen and sulphur and salts of the acids it forms are very largely used.

In its chemical nature it shows a strong resemblance to phosphorus, and less distinctly to nitrogen.

Experiments.

I. Heated in the tube (N.B., a very small particle only to be used), the metal gives off vapour, part of which is condensed on the upper cool end of tube. A white ring, and generally also a black or brown ring, is formed alongside, but nearer the heated part of tube. A very unpleasant odour is perceptible whilst the substance is vapourising. The white ring is generally crystalline, As_2O_3; it dissolves in hot water. The brown ring is dull and amorphous, and the black one is shining, but not distinctly crystalline.

II. Heated with sulphur, a yellow-red substance is immediately formed, which sublimes very easily from one part of the tube to another. It is darker whilst hot than when cold. It is a sulphide, and may be As_2S_3 or As_2S_2.

III. Acids have no solvent action.   Nitric acid oxidises it to As_2O_3 or As_2O_5, which dissolves slightly.

Ammonia has no action on the metal, but dissolves the oxide from I. or from III., and also the sulphide in II.   Alkalies, KHO and NaHO, dissolve the metal with evolution of hydrogen ; the oxides and sulphides also dissolve in alkaline solutions.   The hydrogen evolved is not pure, but contains always some AsH_3 ; great care must be taken not to breathe this.

Dry Reactions.

Arsenic can be completely volatilised.   When heated in contact with air, either on charcoal or in an open tube, it burns and forms arsenious anhydride, As_2O_3, which gives a peculiar fume and coloured
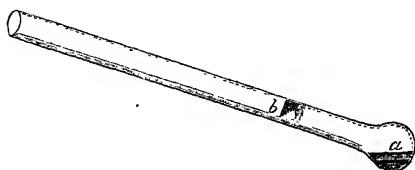

FIG. 81.

flame and most characteristic odour.*   Arsenical compounds give the same indications when heated by themselves on charcoal in the re-ducing flame, and on the addition of sodium carbonate and potassium cyanide, whether the arsenic be present as arsenite or arsenate. The blowpipe experiments should be performed with great caution, since arsenical fumes are poisonous.   The reaction being so very delicate, very small quantities only of the substance need or should be operated upon.

When arsenical compounds are heated in a bulb tube (Fig. 81 or 82), mixed with a proper reducing agent (such as sodium carbonate and charcoal powder or black flux),† metallic arsenic sublimes and is deposited in the shape of a lustrous steel-grey mirror, b, in the upper part of the tube.

As_2O_3, and some arsenites, when heated with a carbonate as $CaCO_3$, calcium carbonate, or K_2CO_3 or Na_2CO_3, give a sublimate of metallic arsenic along with some oxide.   The whole of the arsenic present as arsenite is not given off.

Reactions in Solution.

Chlorine attacks arsenic violently, forming a highly poisonous and volatile liquid, arsenious chloride, $AsCl_3$.   Hydrochloric acid

* The odour of arsenic vapour is said to resemble that of garlic. They are *somewhat* alike.

† See "Reagents," Appendix. This reagent should be a mixture of *dry* soda-lime and charcoal in fine powder. It then answers for Hg, NH_4, As, and Cd compound s. Black flux, made by igniting Rochelle salt, is still better as a reducing agent.

does not act upon arsenic; nitric acid oxidises it to arsenious and arsenic acids, according to the concentration of the acid.

Arsenic forms two oxides, sulphides, &c., and two well characterised series of salts, arsenites and arsenates, as well as arsenides.

A. *Arsenious Compounds.*—A solution of arsenious anhydride, As_2O_3, in dilute hydrochloric acid, or an aqueous solution of an arsenite, K_3AsO_3 potassium arsenite, will give the reactions.

SH_2 (group reagent) produces in an acid solution, especially on gently heating, a lemon-yellow precipitate of arsenious sulphide, As_2S_3, readily soluble in caustic alkalies, in the alkali carbonates and sulphides, forming alkali arsenites and sulpharsenites; it is reprecipitated from any of these solutions on the addition of dilute hydrochloric or other acid. It is almost insoluble in concentrated hydrochloric acid even on boiling, but soluble in nitric acid. On digesting freshly precipitated arsenious sulphide in a solution of hydrogen potassium sulphite, $HKSO_3$, with excess of sulphurous acid, the yellow precipitate is dissolved, and the solution contains potassium metarsenite and potassium thiosulphate, after driving off the excess of sulphurous acid by evaporation, thus:

FIG. 82.

$$2As_2S_3 + 16HKSO_3 = 4KAsO_2 + 6K_2S_2O_3 + S_3 + 7SO_2 + 8OH_2.$$
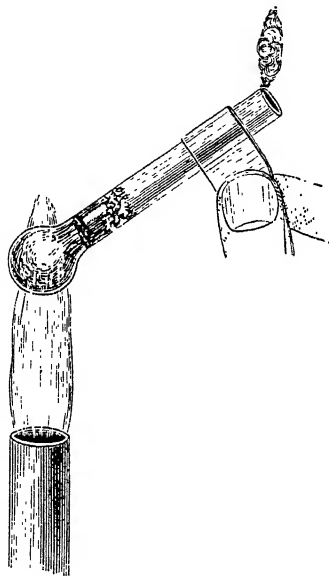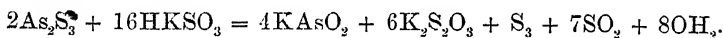
$(NH_4)_2S$, same precipitate, soluble in excess.

$AgNO_3$ produces from a solution of a neutral arsenite, or from a solution of As_2O_3 in water, rendered neutral by cautiously adding ammonium hydroxide, a yellow precipitate of silver arsenite, Ag_3AsO_3, readily soluble in ammonium hydroxide or chloride or nitric acid. The ammoniacal solution of Ag_3AsO_3 and OAg_2, is decomposed on boiling, with separation of metallic silver and formation of silver arsenate, Ag_3AsO_4, thus:

Ag_3AsO_3	$+$	OAg_2	$=$	Ag_3AsO_4	$+$	Ag_2.
Soluble in		Soluble in		Soluble in		Black
NH_4OH.		NH_4OH.		NH_4OH.		precipitate.
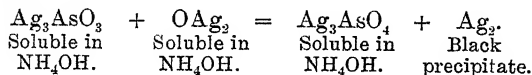
$CuSO_4$ produces a characteristic yellowish green precipitate of hydrogen cupric arsenite, $HCuAsO_3$ (Scheele's green), from a solution of tripotassium arsenite, readily soluble in ammonium hydroxide chloride, or nitric acid.

Magnesium sulphate gives no precipitate in the presence of ammonium chloride.

Reinsch's   Test.—Arsenious oxide and most of its compounds dissolve in HCl, especially when concentrated, $AsCl_3$ being formed. On placing a perfectly clean piece of metallic copper into this, solution and warming, a grey deposit forms on the copper. This consists of arsenic or a compound of As and Cu ; Cu_5As_2. In a concentrated solution the deposit may be black in colour, and will peel off from the copper surface. Antimony is precipitated under similar conditions, so it is necessary to confirm this indication by taking the piece of copper which has become coated by the supposed arsenic film out of the acid solution, drying it by gentle pressure between blotting-paper, and then introducing into a perfectly dry test-tube, and gently heating over a lamp. If arsenic is present a sublimate of arsenious oxide in white crystals will form in the cooler portions of the tube. In the case of large quantities some arsenic will sublime unoxidised, and form a brilliant black or brown film on the glass surface.

Arsenious compounds exert a powerful reducing action when brought in contact with substances capable of parting with oxygen, chlorine, &c. This property is more marked in arsenious than in antimonious compounds.

$AuCl_3$ (auric chloride) produces from an acid solution of As_2O_3 a precipitate of metallic gold, and the reaction is so exact * that the amount of arsenic can be determined quantitatively from the weight of the precipitated gold.

$$4AuCl_3 + 3As_2O_3 + 15OH_2 = 6H_3AsO_4 + 4Au + 12HCl.$$
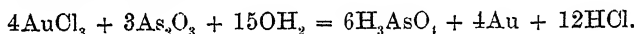
Chlorine water or compounds capable of yielding chlorine, such as a solution of bleaching powder, or of sodium hypochlorite, $NaOCl$ (eau de Javelle), oxidise As_2O_3 rapidly, thus :

$$As_2O_3 + 2Cl_2 + 5OH_2 = 2H_3AsO_4 + 4HCl.$$
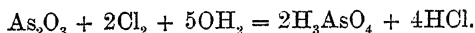
Iodine, dissolved in a solution of potassium iodide, converts a solution of As_2O_3 in excess of hydrogen sodium carbonate into As_2O_5 with formation of an alkali iodide, thus :

$$HNa_2AsO_3 + 2HNaCO_3 + I_2 = HNa_2AsO_4 + 2NaI + OH_2 + 2CO_2.$$

Chlorine, iodine, and bromine act as oxidising agents by decomposing water or a metallic oxide or hydroxide. They form with the hydrogen HCl, HI, HBr, or with a metal the corresponding haloid salt, and the oxygen is transferred to the As_2O_3.

Cupric oxide, or cupric salts, in the presence of sodium or potassium hydroxide, also oxidise or become deoxidised. On adding to a strongly

* All chemical reactions are, of course, *exact* under proper conditions. Where a reaction is spoken of as *partial*, either the physical conditions are not completely known, or more than one path is open for the chemical action to proceed along, and under one condition of temperature it may run more in one direction than another. In many known cases reactions can be reversed by a considerable change of temperature.

alkaline solution of tripotassium arsenite a few drops of cupric sulphate, and warming gently, the blue solution deposits a red precipitate of cuprous oxide, Cu_2O, and leaves tripotassium arsenate, K_3AsO_4 in solution. (Distinction between As_2O_3 and As_2O_5.)

The deoxidising action which arsenious compounds exert upon the higher oxides of chromium and manganese has already been described, (see "Chromium" and "Manganese").

B. *Arsenic Compounds.*—An aqueous solution of tripotassium arsenate, K_3AsO_4, is employed.

SH_2 gives scarcely any precipitate from an acidulated solution of K_3AsO_4, until the solution is heated, and a current of gas passed through for some time. It is difficult to effect complete precipitation even then. The precipitate consists of arsenious sulphide and sulphur. It is preferable to reduce the As_2O_5 first to As_2O_3, by a more powerful reducing agent than SH_2, for example by sulphurous acid: $K_3AsO_4 + H_2SO_3 = K_3AsO_3 + H_2SO_4$, after which sulphuretted hydrogen precipitates the arsenic readily as arsenious sulphide.

$AgNO_3$ gives a reddish brown precipitate of triargentic arsenate, Ag_3AsO_4, soluble in ammonium hydroxide and in nitric acid.

$CuSO_4$ produces a pale greenish blue precipitate of hydrogen cupric arsenate, $HCuAsO_4$, soluble in ammonium hydroxide and nitric acid.

$MgSO_4$ in the presence of ammonium chloride and hydroxide gives a white crystalline precipitate of ammonium magnesium arsenate, NH_4MgAsO_4. (Distinction of As_2O_5 from As_2O_3.)

Fe_2Cl_6 gives a yellowish white precipitate of ferric arsenate, $Fe_2(AsO_4)_2$. Lead acetate gives a white precipitate of lead arsenate, $Pb_3As_2O_8$.

$(NH_4)_2MoO_4$ (ammonium molybdate) with excess of nitric acid gives a yellow precipitate of ammonium arseno-molybdate. This precipitate closely resembles the phosphate one.

Metallic copper does not precipitate metallic arsenic from dilute acid solutions of As_2O_5; but on adding concentrated hydrochloric acid, and heating, a grey film of As_2Cu_5 is obtained. (Distinction between As_2O_3 and As_2O_5.) Some chlorine is liberated, and then attacks the Cu, forming copper chloride.

Arsenic as well as arsenious compounds are capable of oxidising some other compounds, and become themselves reduced either to a ower stage of activity or to arsenic.

Sulphurous acid reduces arsenic acid to arsenious acid.

Sodium thiosulphate deprives arsenious acid of its oxygen, and converts it into As_2S_3, thus:

$$2As(HO)_3 + 3Na_2S_2O_3 = As_2S_3 + 3Na_2SO_4 + 3OH_2.$$
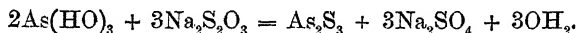
As_2O_3 or As_2O_5 can be detected in solution by the reducing action of hypophosphorous acid, HPO_2, along with SO_2, the arsenic becoming As_2S_3.

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To the arsenic solution one or two drops of PCl_3 (or a little PI_3), or hypophosphorous acid itself, is added, and then a few bubbles of SO_2 gas sent through.   On warming a yellow precipitate of As_2S_3, sometimes with a little sulphur, appears.

Carbon at a red heat removes the oxygen from both oxides of arsenic. —A fragment of arsenious anhydride (white arsenic) is placed in the pointed end, *a*, of a hard glass tube drawn out before the blow-pipe, as seen in Fig. 83.   A splinter of well dried charcoal is next placed in the narrow part of the tube at *b*, somewhat above the fragment of the arsenical compound.   This charcoal is heated over a gas flame or the flame of a spirit lamp.   When the charcoal is well ignited a second
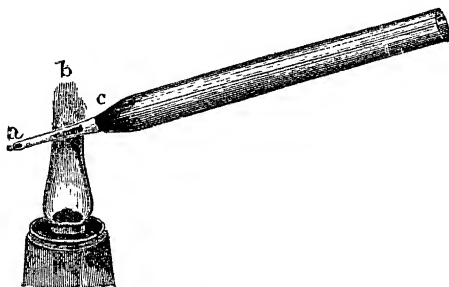
FIG. 83.

flame is applied to the lower end of the tube, in order to volatilise the arsenical compound, the vapour of which, on passing over the glowing charcoal, is deprived of its oxygen, and metallic arsenic is deposited in the form of a shining black mirror on the inside of the tube, above the charcoal at *c*.   The end reaction may be :

$$2As_2O_3 + 6C = As_4 + 6CO_2.$$
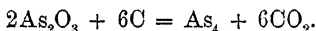
This test is very delicate.   Arsenic in arsenites or arsenates is liberated by mixing perfectly dry charcoal powder, or soda-lime charcoal, with the dry substance, previous to its introduction into the tube, which may have a small bulb blown at its lower end.   The sublimation of metallic arsenic is accompanied by the characteristic garlic-like odour.

KCy reduces arsenical compounds—oxides as well as sulphides— with formation of potassium cyanate or sulphocyanate.   A mixture of potassium cyanide with the arsenical compound is heated in a bulb tube, *a* (Fig. 84).   Metallic arsenic is deposited at *b*.

The changes are expressed as follows :

$$As_2O_3 + 6KCy = 6KCyO + As_4.$$
<div align="center">Potassium
cyanate.</div>

$$2As_2S_3 + 6KCy = 6KCyS + As_4.$$
<div align="center">Potassium
sulphocyanate.</div>
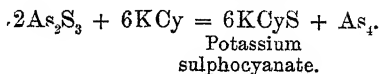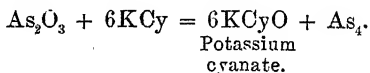
But since commercial potassium cyanide contains potassium cyanate, as well as potassium carbonate (its composition may be expressed as $5KCy + KCyO + xK_2CO_3$), a portion only of the arsenic in As_2S_3 is obtained in the metallic form, and a sulpharsenate is formed which is not reduced by potassium cyanide. On mixing the arsenious sulphide with sulphur, the whole of the arsenic remains behind in the fused mass, as sulpharsenate, and no metallic deposit is obtained. (In the presence of sulphides of Pb, Cu, Ag, Au, Ni, Co, Fe—as, *e.g.*, of FeS_2, in arsenical pyrites, NiS_2, in nickel glance—which are reduced to the metallic state by the action of potassium cyanide, scarcely any arsenical mirror is obtained, because the liberated metallic arsenic
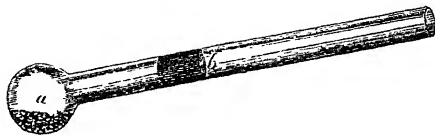
FIG. 84.

would immediately alloy itself with the metals, a portion only of the arsenic being liberated.) These changes are expressed by the equations :

(1) $5As_2S_3 = 3As_2S_5 + As_4$.
(2) $4As_2S_5 + 12K_2CO_3 = 5K_3AsS_4 + 3K_3AsO_4 + 12CO_2$.
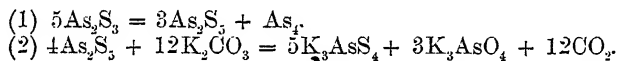
The reduction is conveniently effected by mixing dry arsenious sulphide with one part of potassium cyanide and three parts of sodium carbonate, and introducing the mixture into a piece of combustion tube, *c*, drawn out to a capillary tube as in Fig. 85. A slow current

FIG. 85.

of carbon dioxide is generated from marble and hydrochloric acid in the flask A, Fig. 86, and dried by passing through *b* into the flask B, containing concentrated sulphuric acid, and through the delivery tube *c*, over the mixture in tube C, heated at first gently, till all the moisture has been driven out, and then strongly, almost to fusion— when a mirror of metallic arsenic collects in the neck of the drawn-out tube.

The reaction has this advantage, that no antimony mirror is obtained by the same treatment.

In order, however, to avoid missing the arsenic, either altogether or obtaining only a portion of it, as stated above, it is preferable to treat the arsenious sulphide with a few drops of concentrated nitric acid, and to evaporate with a little sulphuric acid (in order to decompose any metallic nitrates, if present). The sulphuric acid is next neutralised with sodium carbonate, and the mass thoroughly dried

before mixing it with potassium cyanide, and reducing as described. The fused mass retains the antimony, and a good arsenical mirror is obtained, provided no lead, copper, or other reducible metals are present.

Marsh's Test.—Arsenious and arsenic acids are both reduced by nascent hydrogen, which combines with the oxygen of the arsenical oxides to form water, whilst the arsenic in its nascent state, or the very moment it is liberated from the oxygen, also combines with hydrogen to form a gaseous compound of arsenic, called arsenietted
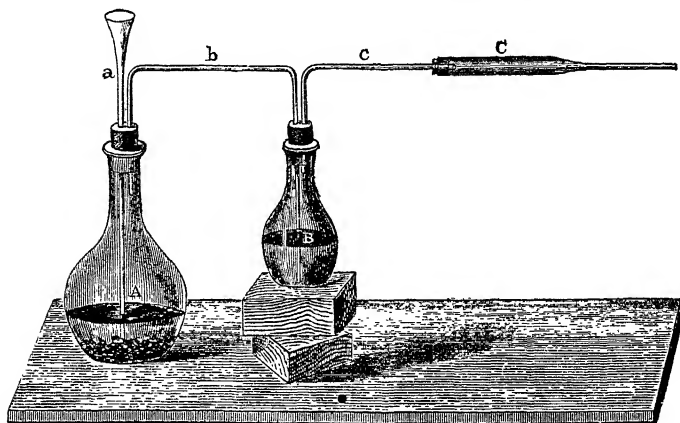
FIG. 86.

hydrogen (arsenious hydride)—AsH_3. This gas is obtained nearly pure by acting with dilute sulphuric acid upon an alloy or compound of zinc and arsenic (Zn_3As_2). The zinc takes the place of hydrogen in the acid, and arsenious hydride is liberated, thus :

$$As_2Zn_3 + 3H_2SO_4 = 3ZnSO_4 + 2AsH_3.$$
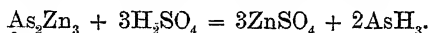
Some other arsenides act in a similar manner. Sodium arsenide decomposes on contact with water, liberating AsH_3, and also forming some As_2H_4, a brownish solid. *Too great care cannot be taken with these arsenic compounds.*

Arsenious hydride is an exceedingly poisonous gas, and the student must on no account attempt to prepare it pure. Its properties, for qualitative purposes, may be studied equally well in a mixture of the gas with much hydrogen.

All experiments with it must be conducted in a fume chamber where a good indraught of air can be obtained. Arsenious hydride possesses a very nauseous odour, and burns with a peculiar livid bluish flame when the jet of hydrogen containing it is lighted. This is due to the combustion of the arsenic to As_2O_3.

Generate hydrogen in a flask, *a*, Fig. 87, from pure zinc (free from arsenic) and pure dilute sulphuric acid. Dry the gas by passing it

over calcium chloride, and connect the drying tube, b, with a piece of hard glass tubing, c, drawn out to a jet.   The hydrogen gas may be ignited at the jet, as soon as it has displaced the air in the generating flask, a; and drying tube, b.   It burns with an almost colourless flame if the zinc and acid be pure.   On introducing a few drops of an arsenious or arsenic solution * through the funnel-tube the flame is seen to change to blue, and on holding a piece of porcelain (*e.g.*, a dish, or the lid of a porcelain crucible) in the flame a black mirror or deposit of metallic arsenic is obtained.   Or the metal may be collected—by heating the glass tube through which the hydrogen
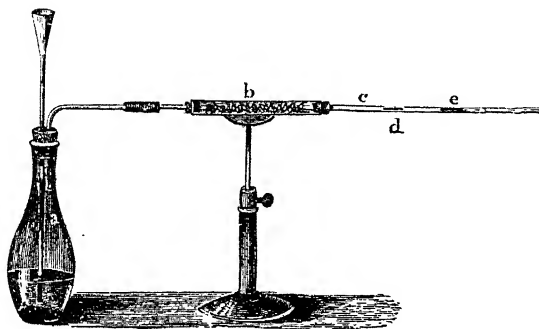
FIG. 87.

passes—in the form of a metallic ring, d, which deposits within the tube immediately in front and in rear of the spot where the glass is heated.   The hydrogen should not be generated too rapidly, if a good ring is to be obtained.

Several arsenical mirrors may be obtained if a long piece of narrow combustion tube, Fig. 88, be employed, which has been contracted in several places by drawing it out in the flame of a blowpipe.   Arsenious hydride is generated in the flask, a, and passing through b, the drying tube, c, and combustion tube, d, issues from the drawn-out jet, where it can be burnt.   The tube d is heated in one or in several places, just before the several drawn-out narrow parts.   An arsenical mirror is obtained a little beyond the heated part of the tube, as seen in Fig. 88.   Little or no arsenious hydride need thus escape from the jet, especially if a slow current only of hydrogen be generated.

The deposition of arsenic in the tube arises from the decomposition of the arsenious hydride, which, at a high temperature, is broken up into arsenic, which is deposited, and hydrogen, which passes on and burns at the jet.   The decomposition which takes place when a cold piece of porcelain is lowered into the flame is readily explained if it be remembered what takes place when some cold porcelain is held in a candle or gas flame.   A deposit of soot is obtained (finely divided

* Any considerable excess of oxidising agents, such as nitric acid, chlorine, &c., should be avoided.   The same holds good for the preparation of SbH_3.

carbon from the hydrocarbons), because the combustion is disturbed, and the temperature of the flame suddenly lowered. The gas can only burn where it is in contact with the air—*i.e.*, on the outside. The arsenious hydride, on passing through the inner portion of the flame, is decomposed by the heat into arsenic vapour and hydrogen gas ; the latter escapes through the outer portion of the flame, and is burnt, arsenic being deposited on the cold porcelain surface. The decomposition of arsenious hydride takes place, even if very little of the gas is mixed with much hydrogen gas. Marsh's test is, therefore, extremely delicate.
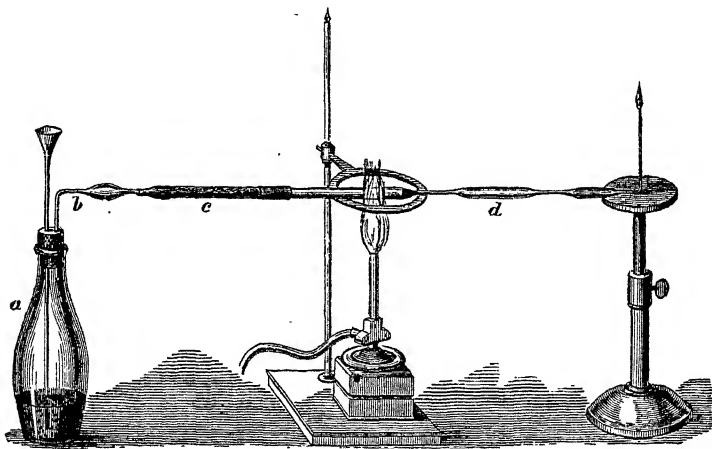
FIG. 88.

It is *absolutely necessary* that both zinc and sulphuric acid be tested first. This is done by generating hydrogen, and allowing the gas to escape by itself for some time through the ignited combustion tube.

Care should also be taken to avoid introducing nitric acid, since arsenious hydride is readily decomposed by this acid. It is therefore preferable to dissolve arsenical compounds in hydrochloric acid, with the addition of a few small crystals of potassium chlorate, and to heat gently till no more chlorous odour is observable.

The metal antimony forms with nascent hydrogen a combustible gas analogous to arsenious hydride, called antimonietted hydrogen (antimonious hydride), SbH_3. It is prepared, though not in a pure condition, by acting with dilute sulphuric or hydrochloric acid upon an alloy of zinc and antimony, thus :

$$Sb_2Zn_3 + 3H_2SO_4 = 3ZnSO_4 + 2SbH_3.$$
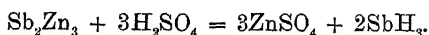
It is obtained mixed with much hydrogen by introducing into a hydrogen apparatus a few drops of an antimony solution ($SbCl_3$, $KSbO_3$, or tartar emetic). The greater part of the antimony, how-

ever, remains behind, precipitated as metal, with perhaps some solid hydride, Sb_2H_4, on the zinc. The hydrogen flame turns at once bluish green, and white fumes of antimonious oxide, Sb_2O_3, ascend into the air. The gas has no particular odour, but is decidedly poisonous. On depressing a cold piece of porcelain into the flame metallic antimony is deposited, and on heating the combustion tube, as in the case of the arsenic experiment, the gas is likewise decomposed into metallic antimony, which collects in the narrowed portions of the tube and forms a dull black mirror, and hydrogen, which escapes and can be burnt at the jet.

Since both arsenic and antimony produce a metallic mirror, such mirror may be due to either metal or to a mixture of the two metals (in which case, however, the more volatile arsenic is deposited further away from the flame, and a part of the antimony is found behind the spot where the glass tube is heated). Further experiments must be made in order to distinguish the arsenic from the antimony in the mirror itself.

This can be done very readily :

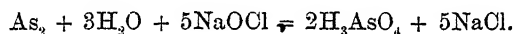1st. By adding to the mirror obtained on cold porcelain a concentrated solution of bleaching powder, or of sodium hypochlorite (eau de Javelle) ; or by simply exposing the mirror to chlorine gas, the arsenical mirror is speedily dissolved ; antimony only after some lengthened exposure, thus :

$$As_2 + 3H_2O + 5NaOCl \rightleftharpoons 2H_3AsO_4 + 5NaCl.$$

2nd. By passing a very slow current of dry sulphuretted hydrogen through the glass tube containing the arsenic and antimony mirror, and applying a gentle heat. The metals are converted into sulphides—arsenic into lemon-yellow arsenious sulphide, and antimony into a black or partly orange-red antimonious sulphide ; and, if both metals are present, the two sulphides appear side by side, the former somewhat in front of the latter, arsenious sulphide being the more volatile of the two. On passing next a current of dry hydrochloric acid gas without the application of heat, antimonious sulphide disappears entirely, being converted into antimonious chloride, which volatilises in the current of hydrochloric acid gas, and may be passed into water and tested for by means of sulphuretted hydrogen. Arsenious sulphide remains unaffected, even if the hydrochloric acid gas be passed over it for some time. The residuary arsenious sulphide dissolves readily in hydrogen ammonium carbonate, HNH_4CO_3.

Antimonious and arsenious hydrides can, moreover, be distinguished from each other by passing them slowly into a solution of silver nitrate, which, acting the part of an oxidising agent, converts arsenious hydride into arsenious acid, thus :

$$AsH_3 + 6AgNO_3 + 3OH_2 = 6Ag + H_3AsO_3 + 6HNO_3.$$

Antimonious hydride is not acted upon like this. The oxidation

extends only to the hydrogen, and not to the antimony, silver taking the place of the hydrogen, thus :

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3.$$
Black precipitate.
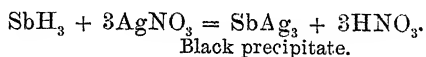
The arsenious acid is separated by filtration from the insoluble $SbAg_3$ and Ag. On cautiously adding to the filtrate a dilute solution of ammonium hydroxide a yellow precipitate of triargentic arsenite is obtained, where the two layers of the ammonium hydroxide and acid solution meet.

The residue is boiled with a solution of tartaric acid, when the antimony compound is acted upon with formation of soluble anti-monious tartrate (?), silver being left behind. Filter ; acidulate the filtrate with dilute hydrochloric acid, and pass sulphuretted hydrogen. An orange precipitate indicates antimony. Another method of detecting the antimony consists in digesting the $SbAg_3$ with yellow ammonium sulphide, when the Sb is dissolved out as sulphantimonite, and can be separated from the filtered solution on addition of HCl as Sb_2S_3.

The hydrogen from Al and KHO can also be employed for Marsh's test, but this must also be tested beforehand.

Another exceedingly delicate reaction for arsenic depends on the facility with which it forms compounds with organic or carbon radicles—viz., methyl, CH_3, or ethyl, C_2H_5. A very small piece of an arsenious compound when heated in a dry tube with a little dry sodium acetate becomes reduced to metallic arsenic, which unites with the methyl groups of the acetate, forming cacodyl :

$\begin{matrix} As(CH_3)_2 \\ As(CH_3)_2 \end{matrix}$ tetramethyl diarsenide, a most minute quantity of which may be recognised by its disagreeable odour.

Electrolytic hydrogen was suggested (*Chem. Soc. Journal*, 1861) instead of using zinc for Marsh's test. The platinum battery-terminals are introduced into the liquid to be examined, and the hydrogen collected and tested as by Marsh's test.

It is valuable in chemico-legal investigations where absolute purity of reagents is necessary.

An electrolytic method (see *Chem. Soc. Journal*, 974, 1903) has been devised for the detection of minute quantities of arsenic contained in foods or any organic preparations. Fig. 89 shows the arrangement of the apparatus. A is a glass vessel with neck ground to fit. Through the neck passes a platinum wire, to which the cathode, B, a cone of perforated platinum foil, is attached. The vessel A dips into a porous jar, C ; outside and at the base of the porous jar is a ring of platinum foil, D, connected to the anode. These stand in a cylindrical glass vessel, in which is dilute sulphuric acid (one acid, seven water).

The outer vessel is to contain cooling water, so that the temperature should be kept below 50°. From the neck of A a tube rises and connects with the drying tube, E, one end of which is closed by a tube stopper, and the other is drawn out to attach to the Marsh tube

of hard glass in which the gas is heated to decompose the AsH_3. The drying tube contains fine granular calcium chloride between loose plugs of cotton-wool, and also small rolls of lead acetate paper —one where the gas enters the drying tube and one in front of the calcium chloride. This is to retain any SH_2.

"The apparatus employed has an apparent resistance of 1·4 ohms, with 7 volts potential difference between ends of pole wires on a current of 5 ampères. This gives about 40 c.c. hydrogen per minute, which furnishes a steady flame of about 2 cm. height."

In working the connections are arranged so that the current passes from D through the porous cell, C, to the platinum cone, B. 30 c.c. of
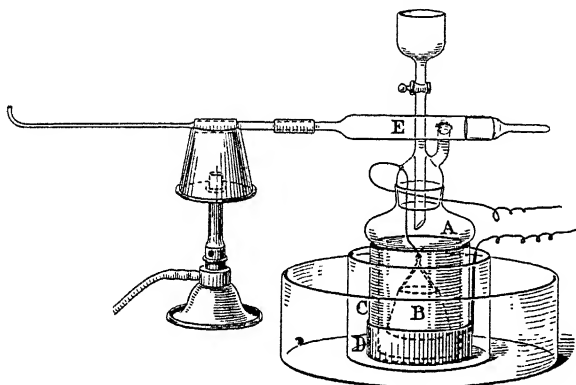
FIG. 89.

the dilute acid are placed in D, and 20 run into the cell through the tap funnel, the stem of which must contain liquid.

At this rate of evolution the apparatus is filled with hydrogen in about ten minutes, when the hydrogen may be lighted and the Bunsen flame under the tube started. If no brown deposit takes place in fifteen minutes the apparatus and acid may be considered free from arsenic, and the liquid to be tested is then run in through the tap funnel. Should the solution contain organic substances it is liable to frothing, to prevent which one or two c.c. of amyl alcohol are previously run into the vessel. At the end of thirty minutes the whole of the arsenic will, as a rule, have been evolved and deposited in the heated tube (see Marsh process, *ante*), which has then to be melted off and sealed up, still full of hydrogen, thus: The stopper of the tap funnel is opened, and a small blowpipe flame applied to the Marsh tube between the flame jet and the deposit. When the tube has melted the end is drawn off. The current is now disconnected, and the tube melted and drawn off just on the other side of the deposit. The sealed tube, with its arsenic deposit, will be 4 to 5 cm. long, and can now be mounted on a white paper card for reference or comparison with standard deposits prepared from known quantities of an arsenic compound.

(4) **GOLD**, Au′ and ‴.—Gold is generally found in the metallic state, and is then readily recognised by its colour, malleability, and other physical characters.   In small quantities it occasionally accompanies metallic sulphides, and is found in some quantity in combination with tellurium.   Pure gold is pale yellow in colour and exceedingly soft, being the most ductile and malleable metal.   It is not affected by air, water, or any single acid, with the exception, perhaps, of Nordhausen sulphuric and selenic acid, H_2SeO_4, at any temperature. It is, however, rapidly acted upon by chlorine, or bromine, or by mixtures of acids which liberate either of these substances (aqua regia), and is dissolved by alkali cyanides in presence of air, a double auri-alkali cyanate being formed.   It unites very readily with mercury, forming a white alloy or amalgam.   It also alloys with most other metals, some of which have a great effect on its colour even when in small quantity—*e.g.*, palladium, arsenic.   Gold may be obtained in an exceedingly finely divided condition either by hammering into gold leaf, or, better, by reducing it in the metallic condition from its salts.   In the latter case it may be obtained so finely divided as to suspend in water for months or even years, forming a red or blue solution, depending on the nature of the reducing agent employed.   This is well shown by passing a few bubbles of PH_3 into a very dilute solution of $AuCl_3$.   It can also be obtained as an almost black powder.

Its atomic weight $= 196·2$. Relative weight, $19·32$. Melting-point, about 900° C.   When melted it gives out a greenish light, almost complementary in tint to its colour in the solid state.

It forms two series of compounds, aurous and auric.

Experiments.

I. Gold leaf contains a little silver, but is most convenient for experiments.

Heated in a tube either in air or vacuum, it melts without change. A piece of gold leaf will melt into the glass of a test-tube.   When looked at it is yellow ; when looked through it appears green.

II. Sulphur has little or no action on pure gold, but gold leaf generally becomes a little duller.

III. Single acids, as HCl, HNO_3, H_2SO_4, have no action.

KHO and NaHO have no action either in solution or when fused.

A mixture of HCl and HNO_3, which evolves chlorine or nitrosyl chloride, dissolves it, forming a yellow solution of $AuCl_3$, which on very careful evaporation leaves a yellow deliquescent solid, $AuCl_3$, which on very moderate heating decomposes into the metal and free chlorine.

Dry Reactions.

When heated on charcoal with sodium carbonate and borax in the reducing flame, gold compounds yield a yellow, very malleable globule of metallic gold.

To detect gold in argentiferous minerals in which it is present

only in minute quantities, and associated with large quantities of other non-volatile metals, the powdered mineral is fused with borax and metallic lead, and the metallic " button " cupelled, as will be described under silver.   The globule of white metal which is left on the cupel is beaten out, and the silver dissolved by digesting with a little nitric acid.   The silver nitrate is poured off, and the gold washed with distilled water.   The black insoluble residue is once more fused on charcoal before the blowpipe, when it assumes the well-known appearance of fine gold.

Old, and sometimes new, silver coins frequently contain a small quantity of gold, which, on dissolving in nitric acid, is left as a black powder.

When an insufficient quantity of silver is present in the " button " (see above) (which may be inferred from its pale yellow colour), from two to four times its own weight of silver should be fused up with it, and the button so obtained beaten out and then treated with nitric acid in order to separate or " part " the gold.—Method of assaying gold.

Reactions in Solution.

Gold when unalloyed is soluble with ease in aqua regia only, forming a solution of auric chloride, $AuCl_3$, which may be employed for studying the reactions in solution.

SH_2 (group reagent) gives from a cold solution a black precipitate of auric sulphide, Au_2S_3, from a boiling solution a brownish precipitate of aurous sulphide, Au_2S.   These precipitates are insoluble in hydrochloric and nitric acids, but dissolve in aqua regia.   They are likewise insoluble in normal ammonium sulphide, but soluble, although with difficulty, in the yellow sulphide, more readily in yellow sodium sulphide, with which they form a sulpho salt, Na_3AuS_3.

$(NH_4)_2S$ and sodium thiosulphate, same precipitate.

KHO, or $NaHO$, produces no precipitate.

NH_4OH produces from a concentrated solution of auric chloride a reddish yellow precipitate of ammonium aurate or fulminating gold, $(NH_3)_2Au_2O_3$, thus:

$$2AuCl_3 + 8NH_4OH = (NH_3)_2Au_2O_3* + 6NH_4Cl + 5OH_2.$$
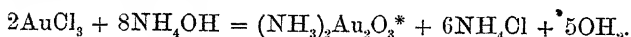
The detection of gold is attended with no difficulty, owing to the facility with which its compounds generally are reduced to the metallic state.   Gold has little affinity for non-metallic elements; the compounds which it forms with them are readily broken up by heat alone, or on being brought into contact with bodies which have more affinity for the metalloids, leaving metallic gold in a finely divided condition as a brown powder, which acquires metallic lustre when dried and rubbed in a mortar.   Hence auric chloride is a powerful oxidising agent, as has already been seen under tin, antimony and arsenic.   The same oxidising action is called into play when $AuCl_3$ comes together with solutions of sulphurous or oxalic acids, ferrous

* This substance is explosive when dry.   It may be a salt of auric acid or a hydrated amino compound.

sulphate, or chloride, cuprous chloride, dissolved in hydrochloric acid, mercurous nitrate, potassium nitrite, sugar in an alkaline liquid, and most other organic substances (*e.g.*, the epidermis). Arsenious, antimonious, and phosphorous hydrides, and even free hydrogen, decompose $AuCl_3$.

The following equations express these changes :

(1) $2AuCl_3$, when ignited splits up into $Au_2 + 3Cl_2$.
(2) Au_2S_3 ,, ,, ,, $Au_2 + S_3$.
(3) $2AuCl_3 + 3H_2SO_3 + 3OH_2$ $= Au_2 + 3H_2SO_4$ $+ 6HCl$.
(4) $2AuCl_3 + 3H_2C_2O_4$ $= Au_2 + 6CO_2$ $+ 6HCl$.
(5) $2AuCl_3 + 6FeCl_2$ $= Au_2 + 3Fe_2Cl_6$.
(6) $2AuCl_3 + 4FeSO_4 + OH_2$ $= Au_2 + Fe_2Cl_6$ $+ Fe_2(SO_4)_3 + H_2SO_4$.
(7) $2AuCl_3 + 3Cu_2Cl_2$ $= Au_2 + 6CuCl_2$.
(8) $2AuCl_3 + 3Hg_2(NO_3)_2$ $= Au_2 + 3Hg_2(NO_3)_2$ $+ 3HgCl_2$.
(9) $2AuCl_3 + 3KNO_2 + 3OH_2$ $= Au_2 + 3KNO_3$ $+ 6HCl$.
(10) $2AuCl_3 + 2AsH_3 + 3OH_2$ $= Au_2 + 2H_3AsO_3$ $+ 6HCl$.
(11) $2AuCl_3 + SbH_3$ $= Au_2 + SbCl_3$ $+ 3HCl$.

In the analysis of a solution containing gold it is usual to remove the gold in the metallic state, by boiling with oxalic and hydrochloric acids, before passing SH_2. The precipitated gold is collected on a filter and fused into a button on charcoal.

There are several other metals also in this group which are removed similarly before continuing the analysis.

Gold is precipitated from a hydrochloric acid solution of $AuCl_3$ by most metals, even by Pt, Ag, and Hg.

PLATINUM, Pt″ and ⁱᵛ. Atomic weight, 194 ; relative weight, 21·50. Melting-point, 1685° C.—This metal is found native, but more frequently alloyed with other metals. The colour of platinum is somewhat between that of tin and silver, being whiter than tin but not so white as silver, or nearly so brilliant. It has about the same hardness as copper, and is eminently ductile and malleable, but somewhat inferior to gold in the latter property. It is much less readily acted upon than gold, either by halogens or acids, and does not amalgamate with mercury, but is corroded by fused caustic alkalies (NaOH and KOH). It is a bad conductor of heat and electricity, and is characterised by its infusibility before the blowpipe and resistance to the usual fluxes. Sulphur has a slight action on platinum when not heated much more than about 500°. Se, Te, and P combine very rapidly, and nearly all metals melt with it more or less easily. Some, as Na, Sn, As, Sb, Pb, attack it vigorously, forming very fusible compounds or alloys. Its reactions in solution need, therefore, only be examined. It forms two well characterised series of salts.

Unalloyed platinum is not attacked by either nitric, hydrochloric, or sulphuric acid, but by aqua regia, with formation of platinic chloride, $PtCl_4$.* The action is slower than with gold. A solution of this salt is employed for studying the reactions of platinum.

* When alloyed with silver, zinc, cadmium, and some other metals, and these alloys are treated with nitric acid, some platinum is dissolved along with the other metals. The amount dissolved varies with the metal, and the amount of platinum in the alloy.

SH_2 (group agent) slowly produces a dark brown precipitate of platinic disulphide, PtS_2. On heating, the precipitate forms more quickly. It is insoluble in nitric or hydrochloric acid, soluble in aqua regia, difficultly soluble in normal ammonium sulphide, more speedily in the yellow sulphide, with which it forms a sulpho salt, $(NH_4)_2PtS_3$. Heated out of contact with air, it is decomposed into PtS and S.

$(NH_4)_2S$, same precipitate.

NH_4Cl produces a light yellow crystalline precipitate of ammonium platinic chloride, $2NH_4Cl,PtCl_4$. From dilute solutions a precipitate is obtained only after evaporation to dryness (on a water-bath). The precipitate is somewhat soluble in water, insoluble in alcohol. (See " Ammonia," *ante*.)

KCl produces a yellow crystalline precipitate of potassium platinic chloride, $2KCl,PtCl_4$, analogous in its appearance and properties to the precipitate just described. (See " Potassium," *ante*.)

NaCl forms with platinic chloride a double chloride, which is, however, soluble in water, and is obtained in needle-shaped crystals by evaporation.

The precipitate produced by platinic chloride with NH_4Cl and KCl serves for the detection and isolation of platinum, and, *vice versâ*, for the detection of ammonium or potassium compounds.

$PtCl_4$ is useful on account of the compounds which it forms with the chlorides of the alkali metals and with the chlorides of many organic bodies, *e.g.*, the so-called alkaloids, such as quinine, nicotine, &c., and amido bodies or bases generally.*

Platinum is capable of forming a lower chloride, platinous chloride, $''Pt''Cl_2$. This salt is obtained by heating platinic chloride for some

* That is, compounds in which the group NH_2 is combined with a more or less complex carbon compound. The double salts with $PtCl_4$ are very characteristic compounds. Whether they arise from the energy of the platinum atom or are a consequence of a rise in valency on the part of the halogen is not yet clearly settled. $PtCl_4$ is difficult to get perfectly pure. The ordinary solution is acid, and probably consists of $PtCl_4 2HCl$, chloroplatinic acid. A constitution as represented by the plan
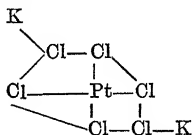
is not at all unreasonable for the potassium salt, as there is plenty of evidence of the halogens acting as triad elements, as in ICl_3 and many other cases.
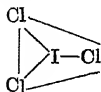
The compound $(NH_4)_2PtS_3$ is also probably of a similar type to the chloroplatinates :
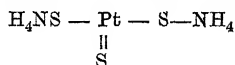
time in an air- or oil-bath up to 240° C., as long as any chlorine is evolved ; or by acting with sulphurous acid upon a solution of platinic chloride, until the latter ceases to give a precipitate with ammonium chloride. $PtCl_2$ is a greenish grey powder, insoluble in water, but soluble in hydrochloric acid.

Several reactions for platinum in solution are based upon the power which its salts possess of oxidising compounds which are chemically unsaturated ; but as platinic salts are not so easily reduced as gold salts, a solution of the latter metal is generally preferred.   After what has been stated under " Gold," the following reactions will be readily understood :

$PtCl_4$ produces with $SnCl_2$ only a dark brownish red colour, owing to the reduction of the platinic to platinous chloride and formation of a platinous tin chloride, $PtCl_2 2SnCl_2 =$

$PtCl_4$ is reduced by $FeSO_4$ only after long-continued boiling.

$PtCl_4$ is reduced to platinum by formic acid, HCO_2H, on heating, if the free acid be neutralised with sodium carbonate.

Metallic zinc precipitates metallic platinum.

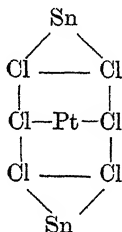$PtCl_2$ is very readily reduced to metallic platinum by $FeSO_4$ and other reducing agents, as oxalates, and is used in photography for this reason.

Hydrazine sulphate precipitates Pt from acid solutions.

$PtCl_2$ is soluble in $PtCl_4$ solution, and gives it a very dark colour.

Whenever platinum and gold are contained in a solution together with other metals of Group II. it is preferable to remove the gold, by means of oxalic acid (which does not reduce platinic chloride), before removing the platinum by evaporation with ammonium chloride.

Gold salts, and sometimes salts of platinum and related metals, are employed in photography for " toning " or imparting a pleasant colour of a more or less permanent character to photographic prints. The main part of the image in a silver print or on a negative is metallic silver.   On contact with the gold solution this becomes first coated with gold and after some time completely replaced by that metal, the silver dissolving.   The colour of the print depends on the stage of completion of this action.

Separation of the metals arsenic, antimony, and tin, whose sulphides are soluble in yellow ammonium sulphide, or in sodium hydroxide.

The precipitate produced by the group reagent is soluble in yellow ammonium sulphide, or in sodium hydroxide, and may consist of three sulphides. If the precipitate be of a dark brown colour, stannous sulphide is indicated; if it be of a fine lemon-yellow colour, the presence of arsenious or stannic sulphide; and if orange-coloured, antimony.

The three sulphides are unequally soluble in hydrogen ammonium carbonate. As_2S_3 dissolves freely, SnS_2 very slightly, and Sb_2S_3 is all but insoluble. On digesting, therefore, the precipitate with hydrogen ammonium carbonate and filtering, arsenic is obtained in the filtrate, and the antimony and tin are left in the residue. In order to separate the remaining two metals, the antimony may be partly converted into antimonious hydride—tin not forming a gaseous compound with hydrogen. For this purpose the two sulphides are dissolved in hydrochloric acid well boiled to expel SH_2, and the solution of the mixed chlorides introduced into a Marsh's apparatus. Antimony is detected by the metallic deposit which antimonious hydride gives on porcelain, insoluble in NaOCl. Tin with some of the antimony is found in the generating flask deposited on the strips of zinc as a greyish black metal. It is removed from the undissolved zinc, dissolved in hot hydrochloric acid (by the aid of a little platinum foil), and the solution tested with mercuric chloride. A white precipitate of mercurous chloride, Hg_2Cl_2, indicates the presence of tin.

The separation of arsenic, antimony, and tin may thus be based upon :

1st. The solubility of As_2O_3 in hydrogen ammonium carbonate.

2nd. The formation of antimonious hydride.

3rd. The precipitation of tin by metallic zinc.

Several other methods of recognising and separating the metals tin, antimony, and arsenic will readily suggest themselves, such as the one which is based upon :

1st. The precipitation of arsenic and antimony in the form of sulphides, by boiling a hydrochloric acid solution of the three metals with sodium thiosulphate, tin remaining in solution.

2nd. By boiling the precipitated As_2S_3 and Sb_2S_3 with hydrogen potassium sulphite and sulphurous acid; As_2S_3 is converted into potassium metarsenite, Sb_2S_3 remains undissolved.

A third method consists in :

1st. Removing the As_2S_3 by boiling with hydrogen ammonium carbonate.

2nd. Solubility of SnS in oxalic acid, Sb_2S_3 being insoluble.

Dissolve the sulphides of tin and antimony in a little strong hydrochloric acid, with the addition of a crystal of potassium chlorate, evaporate the solution till free from chlorine, make it slightly alkaline with NaOH, and add a cold strong solution of oxalic acid, when

the white precipitate thrown down by the NaOH easily redissolves. Pass sulphuretted hydrogen through the solution till no more antimony sulphide comes down ; filter, and wash the precipitate with sulphuretted hydrogen water.   Add to the filtrate some dilute hydrochloric acid, and pass sulphuretted hydrogen for some time ; a yellow precipitate indicates the presence of tin.

A fourth method of recognising arsenic, antimony, and tin is based upon :

The introduction of a solution (in HCl by the aid of $KClO_3$) of the three sulphides into a hydrogen apparatus, and passing the evolved arsenious and antimonious hydride through a solution of silver nitrate ; the tin remains behind precipitated on the zinc.

The solubility of the precipitated $SbAg_3$, in tartaric acid, and precipitation of the antimony by means of sulphuretted hydrogen from a hydrochloric acid solution.

The precipitation of the Ag_3AsO_3 from the silver nitrate solution by means of ammonium hydroxide.

A fifth method of recognising the metals of Group II.B depends upon :

1st. The insolubility of As_2S_3 in strong hydrochloric acid, Sb_2S_3, SnS, and SnS_2 being dissolved.   The presence of arsenic is confirmed by fusion with potassium cyanide and sodium carbonate.

2nd. The precipitation of the antimony on platinum by means of a strip of metallic zinc ; a black stain indicates antimony.

3rd. Dissolving the tin precipitated on the zinc in warm dilute hydrochloric acid, and confirming it by means of mercuric chloride.*

A sixth method depends upon :

1st. The removal of the arsenic from a precipitate of the three sulphides by hydrogen ammonium carbonate.

2nd. The precipitation of the antimony from a solution of the two chlorides by means of pure iron wire, the antimony being separated in the metallic state.   The tin remains in solution as dichloride.

* See also Table II.

CHAPTER XIII.

REACTIONS OF THE METALS IN GROUP I.

THIS group comprises the metals silver and lead and mercury in the form of mercurous compounds which are precipitated from solutions by dilute hydrochloric acid.

(1) **SILVER,** Ag'—atomic weight $= 107\cdot67$, relative weight $10\cdot53$, melting-point about $954°$ C.—is sometimes found in the metallic state in crystals, often on "native" copper; also as sulphide in silver glance, SAg_2, and in combination with antimony, as sulpho salt in the dark red silver ore (pyrargyrite), Ag_3SbS_3; with arsenic as silver sulph-arsenite, in proustite, Ag_3AsS_3; as chloride, AgCl, in horn silver and other ores. Many lead ores, as galena, PbS, contain small quantities of silver.

The colour of metallic silver is white, with a decided red tint, as seen by repeated reflections from the surface.

It is slightly volatile in a stream of air when very highly heated, and dissolves oxygen when melted, which it gives up again on solidifying. Air and water have no action, but ozone slightly oxidises it. Nitric and sulphuric acids dissolve silver, the latter only when heated. Hydrochloric has only a superficial action. Sulphur combines with the metal directly and very easily; most of the tarnishing of silver articles is due to sulphur compounds, especially SH_2, in the air of towns. Many other sulphides also give up their sulphur to it. Its salts with the halogens are very sensitive to light, becoming reduced more or less to lower states of combination.

Some of the salts of silver are reduced by free hydrogen being passed through their solutions. All are reduced to metal under the action of nascent hydrogen.

The chief employment of silver is for coinage, which is generally an alloy of silver and copper. Silver plate also contains copper. Electro-plated articles have a layer of pure silver deposited on their surfaces by galvanic action, the solution employed being, generally, one of potassium silver cyanide. Silver will form either definite alloys or mixtures with most other metals.

Experiments.

I. Silver wire and thin sheet melts easily in a glass tube, and leaves a yellow stain on the glass. Otherwise no change.

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II. Heated with sulphur, the two combine quite energetically, a grey-black crystalline sulphide, Ag_2S, forming, which melts easily, is soft and marks paper. The metal generally glows at the moment of combination.

III. HCl has only a slight surface action, scarcely noticeable.

H_2SO_4 when strong and hot dissolves it, slowly forming Ag_2SO_4 and evolving SO_2. $2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2$. The sulphate is not very soluble in water, and easily crystallises. It bears a high temperature without decomposition.

HNO_3, even when rather dilute, dissolves the metal easily; very strong acid not so rapidly. Oxides of nitrogen are liberated and $AgNO_3$ formed, which crystallises.

Alkalies have no action, but ammonium hydroxide dissolves the oxide and many, if not all, its salts.

Mercury very rapidly dissolves, or amalgamates the metal.

Dry Reactions.

Place a small quantity of powdered silver glance, or the sulphide made in Experiment II., towards the middle of a hard glass tube (combustion tubing of about $\frac{1}{4}$ in. internal diameter, cut with a sharp file into lengths of 5 to 6 ins. answers best). Heat the powder gradually by moving the tube about in a Bunsen gas flame, and lastly heat it strongly towards the centre. By holding the tube in a slightly slanting position a current of air is made to pass over the ignited sulphide; the sulphur becomes oxidised and is carried off as sulphurous anhydride, readily recognisable by its pungent odour. Metallic silver is left, together with a little silver sulphate.

Other volatile bodies, such as antimony, arsenic (selenium and tellurium), which are frequently present in pyritical silver ores, are likewise oxidised, but are to a great extent deposited as As_2O_3 and Sb_2O_3 in the cool part of the tube.

Mix a little of the finely powdered silver glance (or of the roasted ore) with sodium carbonate, and heat upon charcoal under the reducing flame of the blowpipe. A globule of bright metallic silver is left.

Silver ores which contain no other fixed element but silver are reduced on charcoal to the metallic state by a simple fusion with sodium carbonate. Antimony and arsenic, if present, are readily volatilised as metals before the reducing flame. The sulphur combines with the alkali metal.

Silver ores which contain non-volatile metals, such as copper, iron, &c., as in argentiferous fahl ore, and from which the metal silver could not be eliminated before the blowpipe flame, are treated in the following manner:

About ·100 grm. of the finely powdered ore is mixed with its own bulk of powdered borax glass, wrapped up in a small piece of assay lead,* introduced into a cavity made in a good piece of charcoal, and fused under the reducing flame of the blowpipe, at first gently, and afterwards more strongly. The heat is kept up till the whole

* Lead free from silver, prepared from lead acetate.

mass has resolved itself into a metallic button and a clear glassy borax bead, which does not adhere to the charcoal. Should the metallic button, on cooling, present a dull grey surface, indicative of the presence of antimony, it is next heated in the oxidising flame, until, on cooling, it shows a bright surface. It is then detached from the borax, cleaned by a blow with a hammer, and carefully cupelled on some bone-ash pressed into a shallow cavity in a piece of charcoal, the surface being made smooth and thoroughly concave with the round end of a pestle. The button is thoroughly freed from borax, placed in the cupel, and heated in the oxidising flame. The lead is oxidised and absorbed by the porous bone-ash, forming a mass of fused litharge around the metallic bead. If one cupellation does not yield a brilliant white globule of silver—*i.e.*, if the copper has not been entirely removed, a fact which is indicated by a black colour, instead of a pale yellow colour of the litharge, in the cupel—the cupellation of the button must be repeated in a fresh cupel, and the button, if necessary, remelted with a small quantity of assay lead. The silver, not being an oxidisable metal, is obtained in the metallic state.


FIG. 90.

Very small quantities of silver may be separated from lead (as well as from other metals) by cupellation.

Fuse some finely powdered argentiferous galena, PbS,SAg_2, on charcoal before the reducing flame of the blowpipe, either alone or with sodium carbonate. A bead of an alloy of much lead and very little silver is left. Expose this bead on a small cupel (Fig. 90) to the oxidising action of the blowpipe flame. The lead is oxidised and absorbed by the cupel, metallic silver being left.

Chloride of silver may be heated on charcoal with sodium carbonate, when a bead of metallic silver will be left, thus:

$$2AgCl + Na_2CO_3 = 2NaCl + CO_2 + O + Ag_2.*$$
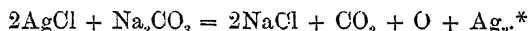
Reactions in Solution.

For the reactions of silver in solution silver nitrate, $AgNO_3$, dissolved in water, is employed.

HCl (group reagent) and soluble chlorides (NaCl, &c.) give a white curdy precipitate of silver chloride, AgCl, which turns violet on exposure to light. The precipitate is insoluble in water and dilute acids; slightly soluble in concentrated nitric acid; readily soluble in ammonium hydroxide, potassium cyanide, and sodium thiosulphate; soluble also to a considerable extent in concentrated hydrochloric acid and in strong solutions of alkali and other chlorides,† more particularly when heated—lithium chloride dissolves more than any other alkali chloride—whence the dissolved silver chloride is, however, reprecipitated on dilution with water.

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* The oxygen represented in this equation combines, of course, with the carbon of the charcoal.

† Silver haloids and cyanide form what are in ignorance termed "double" salts with many other metallic haloid compounds. It is very likely due to a rise in valency of the halogen. Cyanogen can also change its valency.

Collect the precipitated and washed AgCl on a filter and dry in an oven or on a sand-bath. Fuse a portion of the dry salt in a porcelain crucible over a small gas flame. The white powder fuses; it undergoes a physical change only, and leaves on cooling a hard translucent mass, called horn silver.

Place a small piece of zinc on the fused *horn silver*, and add a drop of dilute hydrochloric acid and a little water. The zinc removes the chlorine and leaves metallic silver. The same action takes place when the white curdy precipitate of silver chloride is brought in contact with strips of metallic zinc.

This forms a convenient method of recovering silver from silver residues.

NaHO, or KHO, precipitates silver hydroxide, AgHO, in the form of a brown powder, which on ignition gives off oxygen and water, leaving metallic silver.

(NH_4OH), when gradually added, precipitates silver hydroxide, readily soluble in excess.

SH_2 precipitates black silver sulphide, SAg_2, from acid solutions, insoluble in dilute acids, in alkalies, alkali sulphides, and potassium cyanide; readily soluble in dilute boiling nitric acid, with separation of sulphur.

HI or KI gives a yellowish precipitate of silver iodide, AgI, insoluble in dilute nitric acid and almost so in ammonium hydroxide (distinction between AgCl and AgI).

HBr or KBr gives a yellowish white curdy precipitate of silver bromide, AgBr, insoluble in dilute nitric acid; difficultly soluble in ammonium hydroxide; readily soluble in potassium cyanide or sodium thiosulphate, or potassium iodide.

HCy or KCy gives a white curdy precipitate of silver cyanide, AgCy, soluble in excess of the reagent; insoluble in dilute nitric acid; soluble in ammonium hydroxide, but reprecipitated by dilute nitric acid; soluble in sodium thiosulphate. The precipitate is decomposed by concentrated boiling nitric acid; it is decomposed also when heated by itself in a porcelain crucible, to paracyanogen, metallic silver, and cyanogen gas (distinction from AgCl, AgI, and AgBr).

On placing a bright and clean strip of copper into a solution of silver nitrate, the copper becomes rapidly covered with a lustrous coating of metallic silver, and the solution, after a time, gives no precipitate with hydrochloric acid. The silver is deposited on the copper in the metallic state, and the solution contains now $Cu(NO_3)_2$, an equivalent quantity of copper (63·3 by weight of copper for every 216 of silver) having been dissolved.

Place a small globule of mercury into a concentrated solution of silver nitrate on a watch-glass. The globule of mercury becomes rapidly covered with a crystalline mass, resembling some vegetable growth, termed arborescence. After a time the whole of the silver becomes removed from the solution, which now contains mercuric nitrate, $Hg(NO_3)_2$, in the place of the silver nitrate. Metallic silver is precipitated, and forms with the mercury an amalgam, which is

crystalline.   This action has been known a long time, and the crystalline mass termed a silver tree (*arbor Dianæ*).

Strips of the metals Zn, Fe, Sn, Pb, Mg, and Cd may likewise be employed for the precipitation of metallic silver.

Make a clear solution of one part of grape sugar and six to eight parts of distilled water, and a somewhat dilute solution of silver nitrate. Heat the latter in a test-tube, nearly to boiling, and add the grape sugar solution.   The liquid becomes at once turbid, and a greyish white powder of metallic silver falls to the bottom; or a yellowish white metallic deposit forms on the sides of the test-tube, which, on rubbing with a glass rod, shows bright streaks of metallic silver.   The metallic silver can be filtered off and fused to a brilliant globule.

Most oxygen compounds of silver are not only easily decomposed by a moderately high temperature, but also on contact with organic compounds, such as grape sugar, formic acid, and especially unsaturated substances, as aldehyde.   These substances in all instances become oxidised in some definite manner.

This kind of reaction has found an important practical application in the manufacture of mirrors, speculæ for telescopes, &c.

A number of organic substances, mostly acids, can form compounds or salts with silver.   These on heating decompose, leaving metallic silver, which often retains the shape of the original crystalline substance.

On igniting a few crystals of silver acetate (CH_3CO_2Ag) in a covered porcelain crucible, gently at first, and strongly as soon as no more fumes are given off, a mass of frosted silver is left, having the shape of the original crystals.

(2) **LEAD,** Pb″.—Lead is sometimes found metallic, but more generally in combination with sulphur, as PbS, in galena; also as carbonate, in lead spar or white lead ore, $PbCO_3$; as sulphate, in lead vitriol, $PbSO_4$, in leadhillite, $3PbCO_3,PbSO_4$, and in lanarkite, $PbCO_3,PbSO_4$; as oxychloride, in mendipite, $PbCl_2,2PbO$; as phosphate and oxychloride, in pyromorphite.

The metal has a decided blue colour, and is exceedingly soft; it can be marked by the finger nail, and makes a trail or mark on paper when rubbed over it.   It can be obtained in crystals from fusion and slow cooling.

Its atomic weight $= 206\cdot4$; relative weight, $11\cdot37$; melting-point, $335°$ C; boils between $1450°$ and $1600°$ C.

It oxidises superficially on exposure to air or water, and combines directly with sulphur and the halogens, but not very energetically. Dilute nitric acid dissolves it easily.   Acetic and many other organic acids and also carbonic acid dissolve the metal if it be exposed to air at the same time.   Its oxide, or hydroxide, is also soluble in almost any alkaline solution, such as lime-water; therefore on contact with air and such solutions rapid oxidation of the metal takes place.   Solutions of nitrates, but not of sulphates, act corrosively on the metal.

Sulphuric acid has a very slow action on the metal, a coating of insoluble sulphate forming which acts as a protective varnish. Weak or dilute acids, &c., are more rapid in action than concentrated solutions of reagents, owing to the slight solubility of lead salts generally.

Lead is much employed for acid chambers or vessels to contain strong acids, for pipes, roofing, bullets, &c. The alloy mostly employed is solder—lead and tin. Pewter should contain not more than 10 per cent. lead. Type metal is an alloy of lead with antimony. It is sometimes present in small quantities in other alloys, as bronze, &c., but the qualities it imparts are not, as a rule, desirable.

Storage cells are composed of lead plates, one of which is coated with the peroxide or dioxide, PbO_2, and the other with more or less "spongy" lead. No doubt the oxidation of this spongy or finely divided metal is the origin of the current in the cell. After a cell is charged the condition may be represented by $PbO_2 + H_2O + Pb$ (dilute sulphuric acid being the electrolyte). After a cell has run down the condition is $PbO + H_2O + PbO$, the lead having taken oxygen from an adjacent water molecule, the hydrogen being driven, or wandering, to the negative plate, where it unites with some of the dioxide-oxygen.

Lead may be obtained in a fine powder, which takes fire or glows on contact with air, by gently heating in a partially closed tube lead tartrate, and some other compounds of lead with organic acids.

Experiments.

I. Heated in tube in air, Pb, after melting, changes colour, becomes covered with a grey film ; on heating further the film becomes yellow or reddish when hot and paler on cooling. The changes are due to the formation of oxide. The oxide melts and attacks the glass.

II. Heated with sulphur, combination takes place, the mass becoming red hot and melting ; it is a dull black, brittle solid when cold.

III. Warmed with hydrochloric acid, superficial action takes place, the metal becoming whitened, but little dissolving.

Sulphuric acid when strong also coats the metal with white sulphate ($PbSO_4$), scarcely any dissolving unless the acid be concentrated and boiling, when an acid salt is formed.

Nitric acid dissolves it easily, reddish fumes escaping. On evaporating in dish white crystals of lead nitrate $Pb(NO_3)_2$ are formed. A dilute acid acts quicker than a strong one.

The oxide from I. partly dissolves in HCl, and is converted into white sulphate by H_2SO_4. Nitric acid dissolves it.

Comparatively weak acids, acetic and other organic acids, dissolve lead slowly, especially in contact with air. A white crust of basic or hydrated carbonate may form on the metal.

N.B.—The manufacture of white lead depends upon this behaviour of lead towards organic acids.

Dry Reactions.

The principal blowpipe reaction consists in reducing lead compounds on charcoal to metallic lead, either by themselves, or by the aid of sodium carbonate, or potassium cyanide, and in the yellow incrustation of oxide which they yield, which disappears when heated in the oxidising flame, imparting a blue colour to the flame. The compounds of sulphur, antimony, arsenic, and selenium with lead are somewhat more difficult to reduce than oxy-salts of the metal. The change which takes place when galena is heated with sodium carbonate in a crucible, out of contact with air, is expressed by the equation :

$$7PbS + 4Na_2CO_3 = 4Pb + 3PbSNa_2S + Na_2SO_4 + 4CO_2 ; *$$
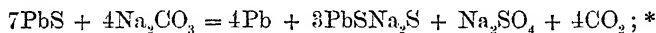
but when heated in contact with air, or in the presence of an oxidising agent such as saltpetre, the loss of lead in the slag is avoided, thus :

$$PbS,Na_2S + 7O + Na_2CO_3 = Pb + 2Na_2SO_4 + CO_2.$$
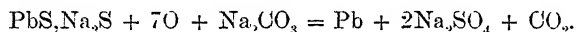
When galena is roasted in a glass tube open at both ends, it is converted into $PbSO_4$, Pb, and SO_2, thus :

$$(1)\ PbS + 2O_2 = PbSO_4.$$
$$(2)\ 2PbS + 3O_2 = 2PbO + 2SO_2.$$
$$(3)\ PbS + 2PbO = 3Pb + SO_2.†$$
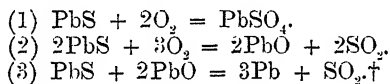
With antimonides or arsenides the action is more complex.

With borax and microcosmic salt, lead compounds give in the outer flame a clear yellowish glass when hot, which is colourless when cold.‡

The presence of antimony, arsenic, and sulphur is indicated, when these ores are heated on charcoal, by the garlic-like odour and fumes of As_2O_3, or Sb_2O_3 ; or in a glass tube open at both ends, white sublimate, fumes, and odour of SO_2.

Reactions in Solution.

For the reactions of lead in solution the nitrate, $Pb(NO_3)_2$, or acetate, $(CH_3COO)_2Pb$, is used, most other lead salts being too insoluble in water.

HCl (group reagent), or soluble chlorides, give, with a not too dilute solution of lead salts, a heavy white precipitate of lead chloride, $PbCl_2$, soluble in much cold water, readily in boiling water, from which the lead chloride crystallises out, on cooling, in fine needles ; less soluble in solutions containing dilute hydrochloric or nitric

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* This double sulphide when heated with iron filings can be reduced to metallic lead, the iron becoming FeS.

† The extraction of lead from galena depends upon these reactions.

‡ All lead minerals, especially the antimonial sulpho salts, boulangerite bournonite, jamesonite, and argentiferous galena, contain more or less silver, as may be ascertained by carefully cupelling the metallic button on charcoal. (Comp. "Silver.")

acid. Ammonium hydroxide converts it into a basic salt, of the composition PbHOCl (lead chlorohydrate)—a white powder almost insoluble in water.

NaHO or KHO precipitates lead hydroxide, $Pb(HO)_2$, soluble in excess of the reagent, especially on heating. The $Pb(HO)_2$ must be viewed as acting the part of a weak acid, compared with the alkali bases KHO and NaHO, or the compound may be looked upon as a substituted hydroxide, thus :

$$Pb\genfrac{}{}{0pt}{}{OH}{OH} + KHO = Pb\genfrac{}{}{0pt}{}{OK}{OH} + H_2O.^*$$
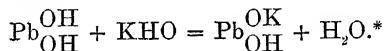
NH_4OH precipitates a white basic salt, insoluble in excess. The precipitate forms only slowly in a solution of lead acetate.

SH_2 precipitates black lead sulphide, PbS, from acid solutions. If a large excess of hydrochloric acid be present the precipitate is reddish brown, consisting of Pb_3SCl_2 (lead sulphodichloride). On diluting considerably with water a black precipitate is obtained.

$(NH_4)_2S$, or soluble sulphides, precipitate black PbS, insoluble in dilute acids, alkalies, and alkali sulphides. Lead sulphide is soluble in hot dilute nitric acid, lead nitrate being formed, with separation of sulphur. Concentrated nitric acid converts it into $PbSO_4$, the oxidation extending to the sulphur as well.

H_2SO_4, and soluble sulphates, precipitate a white sulphate, $PbSO_4$, almost insoluble in water, especially in the presence of excess of dilute sulphuric acid ; insoluble also in cold dilute acids ; soluble in boiling hydrochloric acid, from which lead chloride crystallises out on cooling ; soluble in potassium hydroxide, and readily soluble in concentrated solutions of certain salts, such as sodium thiosulphate, ammonium acetate or tartrate, in the presence of excess of ammonium hydroxide, from which solutions H_2SO_4, in excess, $(NH_4)_2S$, or potassium chromate, precipitate the lead again. Boiling with sodium carbonate converts $PbSO_4$ into an insoluble basic carbonate. Lead sulphate separates from very dilute aqueous solutions very slowly, or only on the addition of alcohol (methylated spirit).

Potassium chromate precipitates yellow lead chromate, $PbCrO_4$ (chrome yellow), readily soluble in potassium or sodium hydroxides, difficultly soluble in dilute nitric acid, insoluble in acetic acid.

Soluble carbonates give a white precipitate of a basic carbonate (a sort of white lead), of varying composition, usually represented as $2PbCO_3$, $Pb(OH)_2$, insoluble in water and in potassium cyanide.

KI gives a yellow precipitate of iodide, PbI_2, soluble in excess of the reagent ; also soluble in much hot water, from which it separates on cooling in beautiful golden-yellow scales. The water solution is colourless.

KCy precipitates white cyanide, $PbCy_2$, insoluble in excess, soluble in dilute nitric acid.

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* This kind of combination may also exist in the case of $Zn(HO)_2$, $Al_2(HO)_6$, and others which dissolve in solutions of alkali hydroxides. Hydrates are relatively either positive or negative.

Soluble phosphates, arsenites, and arsenates, silicates, borates, oxalates, tartrates, citrates, ferro- and ferricyanides give precipitates with lead salts, which are insoluble in water, but soluble in dilute, or strong, nitric acid.   From an analytical point of view, however, these precipitates possess only a secondary interest.

Metallic iron or zinc precipitates lead from its salts.   This is seen very strikingly on dissolving a few ounces (30 or 40 grms.) of lead acetate (sugar of lead) in distilled water, with the addition of a little acetic acid, and suspending in the solution a piece of zinc from a thread.   The zinc becomes covered with a beautiful crystalline deposit of metallic lead, which increases rapidly if the solution be left undisturbed, and acquires the appearance of the branch of a tree (*arbor Saturni*).   The metallic structure can be preserved for days in unaltered beauty.   On removing the precipitated lead from the piece of zinc, the latter is found much corroded and considerably diminished in size and weight.   The lead may be collected on a filter and washed with water, dried, and fused in a crucible, under a covering of borax, to a bright metallic button.   A chemically equivalent weight of zinc to the precipitated lead (*i.e.*, 65 parts by weight of zinc for every 207 of lead) has dissolved, and is found in the solution, in the form of zinc acetate.   The atomic weights of Zn (65) and Pb (207) can be determined roughly, by weighing the metallic zinc, before and after immersion, as well as the precipitated lead.

Heat a little red lead, Pb_3O_4,* in a small porcelain crucible, or in a test-tube, to which a delivery tube is attached.   Oxygen gas is given off, which may be collected in the usual manner over water. The residue is dark yellow, and on cooling turns bright yellow.   It consists of lead oxide, PbO (litharge), according to the equation :

$$2Pb_3O_4 = 6PbO + O_2.$$
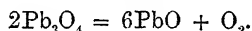
Treat a little Pb_3O_4 with strong hydrochloric acid in a test-tube, and heat gently.   A greenish yellow gas comes off, and lead chloride is produced in the solution.   The gas is readily recognised as chlorine by its property of bleaching litmus paper :

$$Pb_3O_4 + 8HCl = 3PbCl_2 + 4OH_2 + Cl_2.$$
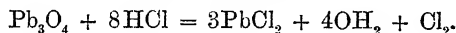
Treat another portion of red lead with dilute nitric acid.   The red colour changes to brown—the colour of lead dioxide, PbO_2.   The reaction is expressed by the equation :

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2OH_2.$$
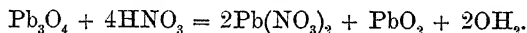
Lead can thus combine either with one or two atoms of oxygen to form PbO or PbO_2 ; and red lead may be regarded as a compound of these two oxides.

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* The composition of commercial red lead is more correctly expressed by the formula Pb_4O_5.

The minerals plattnerite, PbO_2, and minium, Pb_3O_4, represent the corresponding natural oxides.

H_2SO_4 forms with PbO the sulphate, $PbSO_4$, oxygen being given off.

PbO_2 absorbs sulphur dioxide readily, forming $PbSO_4$.

HCl on heating with lead dioxide yields chlorine.

(3) **MERCURY.**—(Mercurosum) $'H'_2$. (See *ante*.)

A solution of mercurous nitrate, $Hg_2(NO_3)_2$, is used, most of the other mercurous salts being insoluble.

HCl (group agent), or soluble chlorides, give a white precipitate of mercurous chloride, Hg_2Cl_2 (calomel), which is insoluble in dilute acids and is blackened by KHO or NH_4OH; the latter converts it into mercurosoammonium chloride, NH_2Hg_2Cl. Mercurous is converted into mercuric chloride by the action of chlorine water. Concentrated hydrochloric acid converts it, upon long-continued boiling, into $HgCl_2$ and grey metallic mercury. Nitric acid oxidises it readily into $HgCl_2$ and $Hg(NO_3)_2$, with evolution of nitrous fumes. Dry Hg_2Cl_2 sublimes unchanged.

NaHO or KHO gives a black precipitate of mercurous oxide, Hg_2O, insoluble in excess.

NH_4OH produces a black precipitate of basic dimercurosoammonium nitrate, $(NH_2HgNO_3)_2Hg_2O$.

The precipitate is insoluble in excess.

SH_2 precipitates black mercurous sulphide, $'Hg'_2S$,* insoluble in excess or in dilute acids; soluble in aqua regia or in yellow potassium sulphide. When boiled with concentrated nitric acid, the second atom of mercury in Hg_2S is converted into $Hg(NO_3)_2$, and a white compound of mercuric nitrate and sulphide is formed.

$(NH_4)_2S$ produces the same black precipitate.

A clean strip of metallic copper precipitates metallic mercury from mercurous solutions, cupric nitrate being left in solution. On gently rubbing the greyish deposit with a piece of wash-leather the surface becomes bright and shining like silver. The more electropositive metals, Bi, Cd, Cu, Fe, Pb, Zn, precipitate the less electropositive metal Hg.

Sulphurous acid, ferrous sulphate, or stannous chloride produce a grey precipitate of metallic mercury. On decanting the liquid and boiling the grey deposit with hydrochloric acid distinct metallic globules are obtained. The changes may be expressed thus:

$$Hg_2(NO_3)_2 + H_2SO_3 + OH_2 = 2Hg + 2HNO_3 + H_2SO_4.$$
$$3Hg_2(NO_3)_2 + 6FeSO_4 = 6Hg + 2Fe_2(SO_4)_3 + Fe_2(NO_3)_6.$$
$$Hg_2(NO_3)_2 + SnCl_2 + 2HCl = 2Hg + SnCl_4 + 2HNO_3.$$
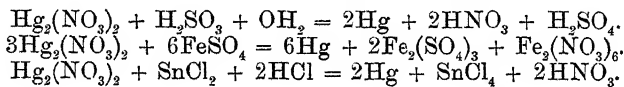
Mercurous salts thus act the part of oxidising agents, when coming in contact with more powerful reducing agents.

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* The substance appears to be a mixture of mercuric sulphide and mercury, as is shown by the ready action which concentrated nitric acid has upon it.

A method of separating the metals of Group I. will readily suggest itself from the following facts:

1st. The solubility of $PbCl_2$ in boiling water.

2nd. The solubility of $AgCl$ in NH_4OH.

3rd. The conversion of the Hg_2Cl_2 into black NH_2Hg_2Cl by the action of NH_4OH.

Table I. in the analytical tables embodies this method of separation, but this is not the only plan, and the student should be exercised in devising other methods.

Before proceeding to the study of the reactions for acids the student will do well to tabulate in a concise way the knowledge gained of all the metallic oxides, hydroxides, sulphides, carbonates, neutral as well as basic, &c., and remember the reactions to some extent, at any rate so as to be able to make use of them to evolve other methods of separation therefrom.

Much precise information will be gained by working out in a tabular form illustrated by equations:

(1) The solubility of all the metals hitherto treated of—

(*a*) In dilute and concentrated hydrochloric acid.

(*b*) In dilute and concentrated nitric acid.

(*c*) In dilute and concentrated sulphuric acid.

(*d*) In aqua regia.

(2) The solubility of the metallic oxides and sulphides obtained by double decomposition in solution, in the different acids, in caustic alkalies, and in alkali sulphides.

CHAPTER XIV.

NON-METALLIC ELEMENTS.

THE non-metals are more varied in physical character than the metals. Some are solids but lack any general property, like metallic lustre; one at least is liquid, and some are gases at common temperatures. They are as a rule bad conductors of heat and electricity, but to this there are exceptions. There is a peculiarity very evident amongst non-metals which is not so much known amongst metals, in that some of them under certain conditions can exist in very different physical states, and this difference in physical state is to some extent attended by a considerable difference in their chemical behaviour. They are said to form allotropic varieties.

CARBON, C'', [iv]. Varieties: a, diamond; β, graphite; γ, charcoal. Atomic weight, 11·97. Vapour density undetermined; not volatile at any known temperature. Specific gravity: diamond, 3·52; graphite, 2·17; charcoal, various, depending on source, from 1·1 to 1·5.—Diamond is the hardest body known. Wood-charcoal is friable, and marks paper with a dull black streak. Graphite makes a shiny and not quite black mark. Cokes, from coal, and gas carbon do not mark paper. Melting-point of carbon unknown; fusible and volatilised in the electric furnace only. Carbon occurs in nature in two distinct crystalline modifications as diamond and graphite. The several modifications exhibit great diversities of colour, lustre, transparency, hardness, and power of conducting heat and electricity. With the exception probably of melted iron, C is insoluble in all known solvents.

γ-Carbon when subjected to a red heat burns in the air or oxygen with production of carbon dioxide; the more compact forms of carbon, graphite, or gas carbon burn with difficulty in the air alone. a-C, or diamond, will not burn even at a red heat in air, but readily in pure oxygen. Graphite or diamond is not attacked by strong nitric acid, but charcoal is oxidised. (See *ante.*)

SILICON, Si^{iv}. Varieties: a, adamantine; β, graphitic; γ, amorphous. Atomic weight, 28. Specific gravity, $a = 2·19$ to $2·49$; β (graphitic) $= 2·00$.—This element, although widely distributed in nature, is never found in the free state, but chiefly in combination with oxygen,

in the crystalline condition as quartz, &c., and in the amorphous condition as opal, flint, &c.

Silicon exists in cast iron in conditions perhaps analogous to the states in which carbon exists in that substance, that is, both combined and in solid solution.

It is supposed to melt between the melting-points of cast iron and steel, but this is doubtful.

Amorphous silicon is a dark brown powder which soils the fingers. When heated in the air it takes fire, burning to SiO_2. Heated in a vacuum, it becomes denser and assumes a graphitic appearance, after which it oxidises much less rapidly on heating in air.

It may be easily obtained by heating sand, SiO_2, with magnesium filings, and, after cooling, washing the product with very dilute HCl.

Hydrofluoric is the only acid which singly attacks silicon.

Heated with KHO or NaHO, silicates are formed, with evolution of hydrogen: $Si + 4KHO = Si(KO)_4 + 2H_2$.

Many metals when in a fused state dissolve and usually combine with silicon—for instance, iron, aluminium, magnesium, and others. On cooling, the Si, or a compound, a silicide, crystallises out to some extent, and may be isolated by treating the metal with an acid, as dilute HCl.

Some silicon steels and silicon bronzes are used to a limited extent.

Silicon combines directly with halogens and also with sulphur at a high temperature. From the silicon chlorides carbon compounds have been formed—so-called organo silicon compounds. From these haloid compounds silicon is obtainable by the action of the alkali metals.

Experiments.

I. Sand is the most abundant silicon compound. It is SiO_2, and undergoes no change when heated. Acids and most other reagents have little or no action upon it.

II. Fine sand mixed with magnesium powder or filings and heated in a tube is reduced to silicon and a compound of magnesium and silicon, $SiMg_2$. The mixture gets very hot during the reaction, and often flies out of the tube. 1 grm. fine sand and ·25 grm. Mg filings will be enough at once. On putting the product into dilute HCl hydrogen and SiH_4 are given off, and the SiH_4 generally takes fire. A brown powder settles down, which should be washed once with very dilute HCl and then with alcohol and dried.

The brown amorphous Si may be (i) heated in a tube in air—it should glow; (ii) heated with NaOH—hydrogen should be evolved.

BORON, B′, ^{iii}; a, β, γ. Atomic weight, 10·94. Specific gravity, 2·53.—Boron occurs in nature in borax and boracic acid; never in the free state. Three varieties of boron are known—amorphous, χ; monoclinic, β; quadratic, a. The latter variety is very hard. Some of these varieties have been obtained by dissolving boron in melted

metals—for instance, aluminium—and there is some doubt whether all the solvent metal has been quite removed. Amorphous boron when unignited is slightly soluble in water, but not in water containing acids or salts.

Amorphous boron is a brown powder which does not oxidise in the air or in oxygen gas at ordinary temperatures, but at about 300° C. it burns, the product being boric oxide or anhydride, B_2O_3.

Boron unites with nitrogen, the halogens, and sulphur directly, and also with some metals. It forms three classes of compounds, direct binary compounds of boron and another element and two oxidation stages.

This element is not used as such, but its compounds with oxygen are largely employed.

Experiments.

The oxide B_2O_3 is the most common oxygen compound; it is contained in borax, which is much employed as a flux for soldering.

I. When heated, B_2O_3 simply melts; no further change takes place.

It dissolves in water, acids, and alkalies, but without any characteristic reactions.

The solution in water is very faintly acid, if at all. Turmeric paper turns brown, as it does with an alkali. It distils rapidly with steam, and can thus be evaporated away.

II. The acid is obtained by making a strong solution of borax, $B_4O_7Na_2$, in water and adding HCl. White crystals quickly form. If the water be poured away and alcohol added to the crystals they dissolve. The alcohol solution, warmed in a test-tube and the alcohol vapour set alight, burns with a green-edged flame. This distinguishes boron, or boric acid, from copper or barium, neither of which is carried up in alcohol vapour.

III. Amorphous boron may be obtained in a similar way to silicon, by heating a mixture of dry borax or B_2O_3 with magnesium filings in a strong tube. The action is energetic. After cooling the product is to be treated with very dilute HCl once or twice, and then washed with alcohol. It is a brown powder after drying.

IV. Heated in air in an open tube, it burns, forming B_2O_3.

OXYGEN, O'', α and β (see *ante*). Atomic weight, 15·96 ; liquid under ordinary pressure at $-193°$. Specific gravity, α liquid, 0·979–0·989 ; as gas, 1·105 (air$=1$); 1 litre$=1·429$ grms. Oxygen occurs in nature, in the free state in the atmosphere in immense quantity combined with metals, as oxides, silicates, carbonates, &c. Although the absolute amount of free oxygen contained in the air is very great, the proportion which the free oxygen bears to that in a state of combination is but very small.

α-Oxygen dissolves appreciably in water ; some metals also absorb oxygen when in the molten state, and give it off again on cooling— *e.g.*, silver. From the energy of its chemical combinations with other substances, oxygen is very easy to distinguish. It forms

compounds with nearly every other elementary substance, in many cases directly.

Substances that burn in air burn in oxygen with increased brilliancy, such as phosphorus, carbon, sulphur, &c.

Free oxygen is absorbed by pyrogallic acid rendered slightly alkaline, and this test is used in gas analysis. The solution rapidly turns brown when much oxygen is present.*

Ozone (see *ante*) is formed by the silent electric discharge; by slow oxidation of phosphorus; by some gases burning in excess of air.

One of the most characteristic tests for ozone is its effect on mercury. The metal at once loses its mobility, and adheres to the surface of the glass in a thin mirror. A single bubble of oxygen containing ozone will alter the appearance of several pounds of mercury, taking away its lustre and the convexity of its surface. Free α-oxygen has no action on potassium iodide, whereas β-O decomposes it into free iodine and potassium hydroxide. Potassium iodide and starch paste, or paper smeared over with a mixture of the two, when exposed to β-oxygen, becomes of a purple or deep blue colour, due to the liberated iodine combining with the starch.

SULPHUR, S'', [iv], [vi] (see *ante*). Several varieties. Atomic weight, 31·98. Specific gravity, α (rhombic) = 2·07; β (monoclinic) = 1·96; γ (amorphous) = 1·92. Melting-point depends on variety, ranging between 112° C. and 120° C.; solidifies, 114° C. Boiling-point, 440° C.—Is found in nature in the free or native state in the neighbourhood of extinct as well as active volcanoes, in Sicily, and many other places.

It occurs in commerce either in sticks, known as roll sulphur, or in the amorphous state as a pale yellow powder, known as flowers or flour of sulphur.

Sulphur is best recognised by means of its two well-known oxidation products, sulphurous and sulphuric oxide, SO_2, SO_3; oxides of the forms S_2O_3 and S_2O_7 also exist, but are very unstable.

NITROGEN, N[i], [iii], [v]. Atomic weight, 14. Specific gravity, 0·963. Specific gravity of liquid at 0° C. and 275 atmospheres pressure = 0·37; liquid under ordinary pressure at −193°–200°. 1 litre weighs 1·245 grms.—Nitrogen exists in the air in the free state

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* A solution of copper oxide in ammonia, rendered colourless by digestion with excess of metallic copper; otherwise a solution of cuprous oxide in ammonia, absorbs oxygen and turns blue. This is a very delicate test for free oxygen. The reagent is best made by dissolving cupric chloride in strong HCl, and boiling the solution with some copper turnings. It will produce a dark brown solution, which is thrown into a considerable quantity of water that has previously been boiled to expel air, and then cooled. A white precipitate of Cu_2Cl_2 is formed, which may be washed with dilute alcohol and dried. It will then keep any time. A small quantity is then dissolved in strong ammonia in a small bottle kept quite full and also containing copper turnings. Taking out the stopper in the air will be sufficient to cause a blue coloration. Ferrous oxalate dissolved in an alkali oxalate also absorbs O rapidly, turning dark red.

mechanically mixed with oxygen ; and combined in certain salts, as nitrates, and also in both vegetable and, especially, animal substances.

It may be obtained pure from nitrites and ammonia salts by the reaction: $KNO_2 + NH_4Cl = KCl + 2H_2O + N_2$. (See *ante*.)

PHOSPHORUS, P′, $^{iii, v}$, α, β, γ. Atomic weight, 30·96. Vapour density, 4·35 to 4·50. Specific gravity, ordinary waxy, a, 1·76–1·83 ; red, β, 2·20 ; metalline, γ, 2·34. Melting-point, 44°.—Phosphorus never occurs in nature in the free state, but chiefly in combination with lime and alumina as phosphates.* In commerce it is obtainable in two forms—viz., common colourless or octahedral phosphorus, usually in the form of sticks, and the red or amorphous phosphorus, in the form of powder.

Ordinary phosphorus is nearly insoluble in water, readily soluble in chloride of sulphur and carbon disulphide, from which crystals of phosphorus can be obtained on evaporation, and in most organic liquids, as ether, alcohol, benzene, vegetable and mineral oils, &c. &c. The luminosity of free phosphorus in the dark, and the peculiar smell of this element produced when it is exposed to air and slowly oxidising, renders its detection comparatively easy. Phosphorus is a bad conductor of electricity either in the fluid or solid state. It is highly poisonous. Ordinary, or a-phosphorus, is extremely inflammable, taking fire in the open air, often spontaneously ; it burns with a yellowish green flame, emitting dense white fumes of phosphoric anhydride and some lower oxides. It is not attacked by strong hydrochloric acid except under 'pressure, but concentrated sulphuric acid is reduced by it to sulphurous anhydride, and on heating even to sulphur. Nitric acid oxidises it to phosphoric acid on long-continued boiling.

Very minute traces of free phosphorus may be detected by the characteristic flame, like that of phosphoretted hydrogen, which is evolved when the substance containing it is exposed to the action of nascent hydrogen. The substance is introduced into a flask fitted up like Marsh's apparatus for the detection of arsenic. If phosphorus be present, the evolved gas contains phosphoretted hydrogen, and will burn with a green flame when the end of the jet is kept cool. The gases may also be aspirated through a nitric acid solution of ammonium molybdate, when a characteristic yellow precipitate will be formed, or through a solution of $AuCl_3$, when an intense red colour will be produced by the reduction of metallic gold in a fine state of division. A piece of blotting-paper moistened with silver nitrate and held in the gas will become brown or black when only most minute traces of phosphorus are present. Sulphides must, of course, be absent.

Red or β-phosphorus is obtained by heating a-phosphorus to between 300° and 400°, therefore under pressure, or, better, by melting with a little iodine. A certain small quantity of iodide of phosphorus is formed, and by some molecular agitation much ordinary phosphorus is converted into the red variety. It is insoluble in all

* See " Calcium " and " Aluminium " for minerals.

solvents, and not acted upon by oxygen at the ordinary temperature. It burns like α-phosphorus, however, when heated in the air to about $300°$ C. Chlorine or iodine combine with it directly, and if water be present both hypophosphorous acid, HPO_2, phosphoric acid, and a haloid acid are produced.

The phosphoric acid may then be tested for by a nitric acid solution of molybdate. A very small particle of β-phosphorus, a bit of safety-matchbox striker, will give the reactions of phosphorus on warming with a small crystal of iodine and one drop of water in a test-tube, and after the reaction a few drops of nitric acid and ammonium molybdate added. Phosphorus is contained in some alloys known as phosphor bronzes.

Some pig-irons contain as much as 2 per cent. of this element.

Experiments.

Waxy phosphorus is sold in sticks or rods and kept under water, they have generally a whitish coating, supposed to be produced by the action of light. Amorphous, or red, phosphorus is a powder of more or less purple-red colour.

Very great care must be taken in handling waxy phosphorus, as it is liable to take fire in air and the burn is difficult to heal. It must be cut whilst wet with water and dried by a little blotting-paper. For the experiments a very small piece, not larger than an ordinary match head, may be taken. The same amount will also be enough of the *red phosphorus.*

I. Heated in a tube, *ordinary* P melts on very gently warming and gives off a peculiar odour. It very quickly takes fire and gives a thick white smoke. A piece of blue litmus paper held in this smoke as it escapes from the upper end of the tube is reddened. The tube will have yellowish or red rings left in it above where the piece of P was. These are due to some of the red or β-P formed by some phosphorus vapour being heated to the "changing" temperature. β-phosphorus requires to be much more strongly heated before it takes fire. The same products are formed as it burns.

II. A tiny piece of waxy P dropped into about half an inch of turpentine or sulphide of carbon in a test-tube dissolves almost immediately on contact. On allowing the solution to evaporate in a dish or pouring a few drops on blotting-paper it takes fire spontaneously when the solvent has evaporated.

III. Sulphuric acid, when concentrated and boiled on phosphorus, oxidises it, SO_2, and sometimes even sulphur, being liberated. Strong nitric oxidises and dissolves both kinds of phosphorus. Red fumes of oxides of nitrogen are evolved and phosphoric acid formed. On evaporating the nitric away a clear glassy substance, metaphosphoric acid, is left. Hydrochloric acid has no action on either kind of phosphorus.

IV. A small piece of dry α-phosphorus, very gently warmed in a test-tube with a tiny crystal of iodine, rapidly undergoes the change into the β modification. At the same time some phosphorus iodide,

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PI_2, is formed. If any moisture be present this decomposes, and fumes of HI escape from the tube.

V. Alkalies, including CaO and BaO, but not ammonia, when warmed with a-phosphorus give off PH_3, and a salt of H_3PO_2 is formed. This should be done in a test-tube only. It may have a cork and delivery tube.

$$3Ba(OH)_2 + 2P_4 + 6H_2O = 3Ba(H_2PO_2)_2 + 2PH_3.$$
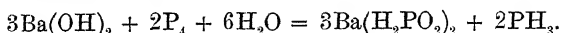
VI. Phosphorus, either a or β, combines directly with metals. Place a small particle of red phosphorus on platinum foil; heat over the flame. At about the temperature of change of state a phosphide of platinum forms and melts a hole.

The Halogens.—The four substances F, Cl, Br, I form a very well marked group of elements. This is shown by both their physical and chemical properties.

Boiling-points of the halogens in absolute degrees C. :

$$\begin{aligned}
&F\ \ \ 87° = -196° \\
&Cl\ 240° = -\ \ 33° \\
&Br\ 337° = +\ \ 64° \\
&I\ \ \ 460° = +187°
\end{aligned}$$

The "halogens" cannot be obtained, practically, by heating their compounds with the common metals, but the haloid compounds of Au, Pt, Pd, and one or two other metals of that class, are decomposed on heating to redness. Many haloid salts may be electrolysed in water solution and the haloid collected. Most, if not all, haloid salts electrolyse easily in a fused state. The ordinary methods of obtaining Cl, Br, and I depend on the oxidation of the hydrogen compounds. The action of bleaching is the reverse of this, as it depends on the halogen taking hydrogen from water and liberating (probably) active oxygen.

FLUORINE, F'. Atomic weight, 19.—Fluorine occurs in combination with calcium, aluminium, potassium, sodium, &c., in minerals like fluor spar, cryolite, &c. It is also found in the teeth and bones, and in many silicates and phosphates, and hence occurs in soils in small quantities, from whence it is taken up by plants. The hydrogen compound of fluorine is treated of under "Acids."

Fluorine is a gas, under ordinary conditions of temperature, which attacks nearly all substances, metals or non-metals, and many compounds, especially if they contain hydrogen. With oxygen and nitrogen it does not seem to combine.

The most satisfactory method of preparation (isolation) is by the electrolysis of KF in solution in anhydrous HF, at a low temperature in a platinum vessel. Glass vessels cannot be employed at any temperature much above that of boiling oxygen ($-183°$), on account of the formation of SiF_4. On cooling to about $-187°$

fluorine forms a pale yellow liquid of great mobility. At this low temperature nearly all its chemical activity ceases, for silicon, boron, carbon, sulphur, phosphorus, and some other elements are not affected, nor are iodides decomposed, but benzene and turpentine become incandescent, and with hydrogen it explodes.[*]

Liquid fluorine seems to mix in all proportions with liquid air. It does not solidify at $-210°$. Its density is $1\cdot14$; its capillarity is less than that of liquid oxygen; it has no absorption spectrum and is not magnetic.

Experiments.

A most characteristic property of fluorine is its affinity for silicon, whether free or combined. In consequence it attacks glass and all substances containing silicon. The hydrogen compound of fluorine, HF, decomposes silica, SiO_2, the F uniting with the Si.

I. Pound up some fluor spar, CaF_2, or cryolite, $(NaF)_6Al_2F_6$, put in a leaden or platinum dish, and pour on concentrated sulphuric acid. Coat a glass plate with a very thin layer of wax, or paraffin, and scratch with a sharp point some design or words through the wax, and then cover the lead or platinum dish containing the mixture of fluoride and acid with it. Place the dish in a warm place for a short time, take off the plate, warm over a lamp to melt the wax, which can then be wiped off, and the design eaten or etched into the glass should be visible.

The compound formed between fluorine and silicon is SiF_4, a gas which on contact with water decomposes, gelatinous silica being deposited and a complex acid, hydro-fluo-silicic, $2HF,SiF_4$ left in solution.

This acid is sometimes used as a reagent.

CHLORINE, Cl' and $'''$. Atomic weight, $35\cdot37$. Specific gravity, liquid $= 1\cdot33$; gas $= 2\cdot449$ (air $= 1$).—Chlorine never occurs in the free state, but chiefly in combination with the alkali metals, as NaCl, KCl, and also with magnesium. It liquefies under a pressure of 6 atmospheres, at $0°$ C., or at a temperature of $-33°$, at 760 mm. The liquid does not conduct electricity, and is not very active chemically.

Chlorine at ordinary temperatures is a greenish yellow gas, which exerts a poisonous and irritating action on the air passages. It dissolves in about half its volume of cold water, and it is commonly used in this form in the laboratory. The water solution on cooling gives crystals of a hydrate.

Chlorine combines with the metals directly, and with many of the non-metallic elements. Its solution in water decomposes on exposure to light, HCl being formed and oxygen liberated. When heated with steam the same decomposition also takes place.

Chlorine will at elevated temperatures expel oxygen from nearly all the metallic oxides. N.B.—The reverse action can take place. See *ante* (chlorides, &c., heated in air).

[*] Moissan and Dewar, Chem. Soc. Nov. 1897.

The presence of free chlorine is indicated by its powerful odour, its bleaching action on vegetable colours, its action on potassium iodide and starch (formation of blue iodide of starch), and, when in very small quantity, by its secondary oxidising action on a solution of pure ferrous sulphate mixed with ammonium sulphocyanate, NH_4SCy, whereby a deep red colour is produced.

Experiments.

I. Mix 12 grms. salt, NaCl, with 9 manganese dioxide, MnO_2, introduce into a small flask or wide test-tube, moisten with very little
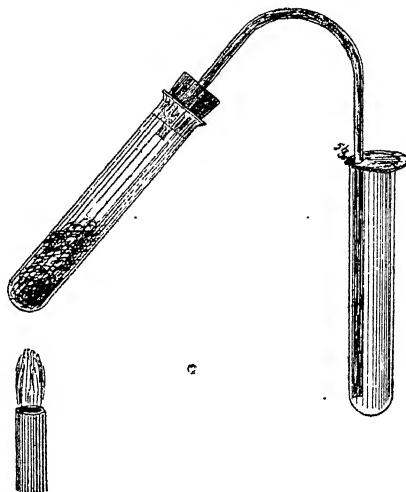

FIG. 91.

water, and then add about 5 c.c. strong sulphuric acid, and insert a cork with tube. The gas can be best collected in dry cylinders or test-tubes by leading the delivery tube to the bottom; the tubes may be covered with watch-glasses. Collect three or four test-tubes full by displacement of air by the heavier gas, and also let the gas bubble through water in a test-tube half full. The water will become coloured yellow-green.

II. In one tube of the gas hold a piece of moist blue litmus paper; it becomes immediately bleached, almost before it has time to turn red.

III. In another drop a small piece of tinfoil; it melts down apparently, and forms a fuming liquid. In the third tube put a very small piece of real gold leaf; this also will be acted upon and combine with the chlorine, and a yellow liquid will result after adding *one* drop of water. In a fourth tube of the gas insert a lighted wax taper; it will be seen to burn very dimly, and give a copious deposit of carbon as soot.

Chlorine, in fact, unites directly with nearly all the elements, the only striking exceptions being carbon and oxygen and nitrogen.

IV. The solution of chlorine in water will also bleach many ordinary colours, such as indigo. Pour a dilute indigo solution into the chlorine water; the blue colour is totally destroyed.

V. Chlorine is stronger chemically than either bromine or iodine. Place a few crystals of potassium bromide in one tube, and some of potassium iodide in another. Now put the delivery tube from the chlorine apparatus into these in succession; one will become reddened by the liberation of bromine, the other nearly black by the liberation of iodine.

BROMINE, Br' and '''. Atomic weight, 72·77. Melts at 7·3° C.; boils at 59·27° C. under 760 mm. Relative weight = 3·15.—Bromine occurs mostly in combination with the alkali metals; and as bromide of silver in Mexico and Chili. At ordinary temperatures bromine is a liquid of deep brown colour, almost black; the vapour has a peculiarly disagreeable odour; in the solid form it is dark grey and crystalline, with a semi-metallic lustre. In both states it is a non-conductor of electricity. It is very volatile; a few drops put into a flask speedily fills it with red vapours. Bromine dissolves sparingly in water, more readily in alcohol, on which it slowly reacts, and in all proportions in ether, carbon disulphide, and chloroform.

Bromine does not unite directly with oxygen; but when passed through a red-hot tube with water vapour, oxygen is set free, and hydrobromic acid is formed. Bromine is the only liquid element at ordinary temperatures except mercury. Bromine and its compounds resemble chlorine and its compounds very closely, although it is not so energetic. It bleaches organic colouring-matters, but less quickly than chlorine does, and combines directly with metals to form bromides, but its action is less powerful than chlorine. Bromine forms only one compound with hydrogen—namely, hydrobromic acid, but, unlike chlorine, they do not unite when brought together in sunlight.

Experiments and Tests.

I. Put a few drops of bromine into a good sized flask; it evaporates without heating and red fumes fill the flask (be careful not to breathe these fumes). Hang in the neck of the flask a strip of moistened blue litmus paper; it will turn red and yellow, and then gradually lose its colour or bleach.

II. Hold for a moment a strip of blotting-paper that has been dipped in a solution of potassium iodide and starch in the neck of the flask; it will be blued, as was the case with iodine and starch. The bromine has liberated the iodine from the potassium and taken its place.

III. Cold solution of NaHO dissolves bromine, the solution containing hypobromite, bromide, and bromate. On evaporating in a dish a white crystalline residue is left.

IV. The solution of NaHO to which bromine has been added bleaches a piece of litmus paper quicker than bromine itself. This is due to NaBrO.

Dilute ammonia dissolves and combines with it, forming bromide. Some nitrogen may be liberated.
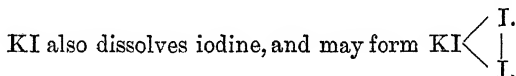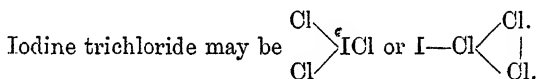
A strip of lead held in bromine vapour or in a solution of bromine, either in water or any other solvent, becomes coated with a pale yellow substance, $PbBr_2$.

IODINE, I′ and ‴. Atomic weight, 126·56. Relative weight, 4·948. Melting-point, 113–115° C. Boiling-point, 187° C.—Iodine is a bad conductor of electricity, and possesses a less penetrating odour than chlorine or bromine.

It occurs in combination with the alkali metals, as iodides of potassium and sodium in kelp; also in several minerals, as iodides of mercury and silver. Much is obtained from Chili saltpetre, wherein it exists, for the most part, as sodium iodide.

Iodine is a crystalline, opaque, shining, blackish-grey solid; it crystallises by sublimation in the rhombic system in the form of prisms. It is sparingly soluble in water, more readily soluble in alcohol and ether, easily in carbon disulphide, and in the solution of an iodide.*

Iodine forms only one compound with hydrogen—viz., hydriodic acid, HI. Iodine combines both with chlorine and bromine in at least two proportions. ICl = iodine monochloride, a liquid, and ICl_3 = iodine trichloride, a solid. The converse compound, ClI_3, can also exist.

Iodine trichloride may be $\begin{matrix} Cl \\ \diagdown \\ Cl \diagup \end{matrix} ICl$ or $I-Cl\begin{matrix} \diagup Cl. \\ | \\ \diagdown Cl. \end{matrix}$

KI also dissolves iodine, and may form $KI\begin{matrix} \diagup I. \\ | \\ \diagdown I. \end{matrix}$

This element has more affinity for oxygen than either Cl or Br, uniting to a slight extent directly, and is readily oxidised by nitric acid, or permanganate and other oxidising agents, forming several well-defined and stable oxides and anhydrides.

Experiments and Tests.

I. Heated gently in a tube, iodine vapourises, even before melting, and gives a fine violet vapour; shining blackish crystals form on the cool parts of tube. The vapour has an irritating effect on the eyes, and a peculiar odour, something like seaweed.

II. A piece of ordinary white paper, or, better, a little blotting-paper with some starch spread on it, held over the upper end of tube, becomes purple-blue in colour.

III. A piece of blotting-paper moistened with silver nitrate or lead acetate, held in the fumes, becomes yellow.

IV. A tiny globule of mercury and a crystal of iodine warmed together in a test-tube unite energetically, and a yellow compound,

* These are no doubt compounds.

HgI_2, sublimes in the tube. The yellow sublimate turns pink on cooling or rubbing.

V. Hydrochloric has no action on iodine.

Sulphuric dissolves it merely; the solution is brown-red.

Nitric, strong, when boiled with iodine, partly oxidises it to a white substance, which may be obtained on evaporating off the acid in a dish; it is mostly iodic acid, HIO_3, but contains a higher oxygen compound as well.

VI. NaHO when gently heated dissolves it readily, forming iodide and iodate, the latter of which rapidly crystallises.

(The iodates are far less soluble than iodides, or even chlorates.)

Warm ammonium hydroxide also dissolves it completely when dilute; when concentrated a brown powder is produced, NHI_2, which is most highly explosive when dry. It must not be made in any quantity. About half a gram (or 10 grains) of iodine and five cubic centimetres of strong ammonia solution are mixed in a small dish. After a few minutes the dark brown liquid can be poured off and replaced by water, and this again poured off after the brown substance has settled. On drying this substance *in small portions on blotting-paper* spontaneously in the air, its explosiveness may be tested by rubbing it gently with a feather or quill pen.

Carbon disulphide is the best solvent for iodine. The solution has the same colour as the vapour of the element; it gives crystals on evaporation.

Turpentine is very energetically acted upon by iodine, especially when warm, much hydriodic acid, HI, being formed.

HYDROGEN, H. Standard of atomic weight (1). Gaseous down to $-234°$ C. At about this temperature it liquefies under ordinary atmospheric pressure. (See *ante.*)

The presence of hydrogen in compounds is usually detected by the formation of water by some process or other. In some inorganic or mineral compounds, as HCl or NH_3, this can be done by heating with some metal, as Na or Zn. As it is not absorbed by liquid reagents, and most other gases excepting N are, it can then be dried by collecting over H_2SO_4, standing a little time, decanting to a tube over dry Hg, a little dry O added, and a wire or strip of Pd, sealed on a glass rod or platinum wire, introduced. The Pd causes the H and O to unite, and the sides of the tube may become moistened from the H_2O formed, or a small piece of dry $CuSO_4$ may be pushed through the Hg, when, if H_2O is formed, it will become blue. In organic compounds the H is always oxidised to water, either by heating in dry oxygen gas or with CuO.

CHAPTER XV.

REACTIONS OF THE ACIDS.

A. INORGANIC ACIDS.

CARBON DIOXIDE, or **CARBONIC ANHYDRIDE,** CO_2 (see *ante*).—Occurs in the atmosphere and in mineral waters. In the combined state it forms a constituent of many minerals, called carbonates, which have for the most part been enumerated in speaking of the natural compounds in which the different metals occur.

CO_2 may be liquefied by about 75 atmospheres pressure at the ordinary temperature. The liquid evaporates very rapidly, with great absorption of heat, solidifying some of the remaining liquid.

The density of the gas $CO_2 = 1 \cdot 519$ (air $= 1$); the liquid at $0° C. = 0 \cdot 9471$ (water $= 1$).

Experiments.

Prepare and collect several large test-tubes * of the gas by acting on $CaCO_3$ with dilute HCl in an arrangement like that figured for chlorine (*which see*). Collect by downward displacement.

I. In one tube introduce a strip of moist blue litmus paper; it will become claret-coloured.

II. Pour lime water into tube; it becomes milky.

$$CaH_2O_2 + CO_2 = CaCO_3 + H_2O.$$
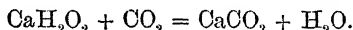
III. Introduce burning taper; it will be extinguished, and the gas does not burn.

IV. Introduce burning magnesium ribbon; it will continue to burn feebly, and black specks of carbon will be found along with MgO in tube. On adding HCl the MgO dissolves, leaving the C.

Potassium or sodium heated on a deflagrating spoon and introduced in gas will glow brightly, also leaving black carbon.

Dry Reactions.

On ignition some carbonates easily lose CO_2, others remain unchanged. The carbonates of the fixed alkali metals are very little

* So-called boiling tubes.

decomposed by heating with a blowpipe flame in a platinum crucible. At very high temperatures they are somewhat volatilised. The acid carbonates of the alkalies are reduced by heat to normal carbonates, with evolution of CO_2. The carbonates of all other metals are decomposed more or less readily into oxides (or metals), carbon dioxide (and oxygen) being given off. Barium and strontium carbonates require the strongest white heat for their decomposition; calcium carbonate requires a strong red heat.

Reactions in Solution.

All normal carbonates—that is, M_2CO_3 or MCO_3—may be divided into:

1st. Carbonates which are soluble in water, consisting of the carbonates of the alkali metals, Li, Na, K, Cs, Rb; they possess an alkaline reaction.

2nd. Carbonates which are insoluble in water; this comprises most other normal carbonates.

3rd. Acid carbonates or normal salts in presence of carbonic acid in solution in water are soluble. They are all, however, precipitated on boiling their solutions, the CO_2 escaping and a normal carbonate being thrown down.

All carbonates are decomposed by dilute acids—organic or mineral (with the exception of HCy and SH_2). The decomposition is marked by effervescence and evolution of CO_2. On passing the evolved gas into a solution of calcium or barium hydroxide, the carbon dioxide forms a white precipitate (soluble in excess of the gas, with formation of acid carbonates).

Metallic sulphites, sulphides, and nitrites are likewise decomposed by dilute acids, with evolution of a gas; but the evolved SO_2, SH_2, or nitrous fumes are readily recognised by their characteristic odour or colour. In order to recognise CO_2 in the presence of SO_2 or SH_2, the gaseous mixture may be first passed through a solution of a chromate or bichromate, or bromine water, or a solution of a cupric or ferric salt, and finally into lime or baryta water. (See also methods of separation of CO_2, SO_2, &c., in Tables.)

CARBON MONOXIDE, CO.—Molecular weight, 28. Relative weight, 0·06799.—The gas (see *ante*) is perfectly neutral to vegetable colours, and sparingly soluble in water, which only dissolves about $\frac{1}{40}$ of its bulk at 15° C. It is rapidly absorbed by cuprous chloride in hydrochloric acid; also by ammoniacal solutions of cuprous salts.

Carbon monoxide is a result of the reduction of CO_2 by carbon and by most metals at a high temperature, or by combustion of carbon or carbon compounds at a high temperature, as when guncotton or similar substances burn. Some metals, as iron, and especially nickel, combine directly with CO, forming peculiar compounds, as $Ni(CO)_4$, nickel carbonyl. The Ni carbonyl compound is formed by gently heating the metal in a stream of CO. The product is a liquid, the vapour of which decomposes below a red heat, bright metallic

nickel depositing. It is difficult to imagine the nickel to be more than divalent in this compound; if so, its constitution ought to be

$$
\begin{array}{c}
CO \\
| \quad \diagdown CO \\
Ni \quad | \\
| \quad \diagup CO \\
CO
\end{array}
$$
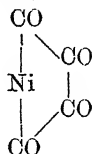
Potassium also combines directly, the compound being very probably $K_2C_2O_2$ or $n(COK)$; it is explosively decomposed by water.

Experiments.

Carbon monoxide can be prepared most easily from formic acid, HCO_2H, by the action of H_2SO_4.

I. The H_2SO_4 is heated gently in a distilling flask or ordinary flask, with cork, tap, funnel, and delivery tube, and the formic acid, or a formate, dropped slowly in. CO is evolved, and may be collected in several tubes over water.

CO is very poisonous; great care must be taken not to breathe any.

II. To one tube introduce blue litmus; it should be unchanged.

III. Introduce a lighted taper; it becomes extinguished, but the gas burns with a blue flame at mouth of tube.

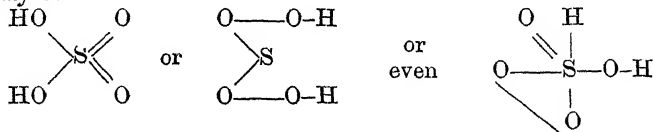IV. Ignite *another* tube of the gas, and then pour in some baryta or lime water.

V. Pour lime or baryta water into a tube of the CO. It should not become milky, whilst in IV? it will, owing to $2CO + O_2 = 2CO_2$, the action taking place when CO burns.

VI. Transfer a tube of CO from the water to a small dish in which a solution of Cu_2Cl_2 in HCl has been placed; the liquid will rise in the test-tube as the CO is absorbed.

SULPHURIC ACID, H_2SO_4, is a very strong acid, and is capable of displacing, within a moderate range of temperature, almost all other acids from saline compounds.

It forms with bases a series of very important salts—the sulphates, some of which have already been enumerated in treating of the natural compounds of the various metals.

The acid is derived from the oxide SO_3, which is produced to a small extent when sulphur is burnt in oxygen. SO_2, sulphur dioxide, also forms SO_3 when heated along with air in contact with platinum. This may be seen by introducing a red-hot platinum wire into a mixture of SO_2 and air or oxygen. It combines with water to form H_2SO_4. The precise "structure" of this substance is not known. It may be

$$
\begin{array}{ccc}
HO \quad\diagdown \!\! S \!\!\diagup\!\!\!= \!\! O \\
HO \quad\diagup \quad\quad O
\end{array}
\quad or \quad
\begin{array}{c}
O\!\!-\!\!-\!\!O\!\!-\!\!H \\
\diagup\! S \\
O\!\!-\!\!-\!\!O\!\!-\!\!H
\end{array}
\quad \begin{array}{c}or\\even\end{array}
\quad
\begin{array}{c}
O \quad H \\
\diagdown\!\!| \\
O\!\!-\!\!-\!\!S\!\!-\!\!O\!\!-\!\!H \\
| \\
O
\end{array}
$$

The probability is in favour of the first.

On a large scale the acid is made by the oxidising action of nitric acid, and oxides of nitrogen, on SO_2. This action can be repeated in a test-tube. Place a few drops of strong nitric acid in a test-tube and then drive in SO_2 gas. Red fumes will first appear, due to the action :

$$SO_2 + 2HNO_3 = \underbrace{SO_3 + H_2O} + N_2O_4.$$
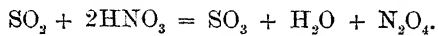
. If the SO_2 supply be continued the red fumes cease and white crystals form on the tube, but if some water be added the crystals will disappear and a further quantity of H_2SO_4 will form. The white crystals are $SO_3N_2O_2$,[*] which with water give $SO_3H_2O + N_2O_2$. The latter escapes, mixes with air, and becomes N_2O_4. If plenty of water be present at the beginning none of these crystals are formed but N_2O_2. In the sulphuric acid manufacture this N_2O_2 is brought in contact with air, so that it can act as a carrier of oxygen to the SO_2.

On heating the liquid in the test-tube until whitish fumes begin to form at the mouth of the tube all the excess of water and oxides of nitrogen are driven off, and a few drops of strong sulphuric acid (oil of vitriol) will be left (see *ante*).

The action of this on a piece of filter paper or sugar should be noticed. The paper will turn black and a hole appear in it. The sugar also will blacken. Both actions are due to the abstraction of the oxygen and hydrogen from these organic substances and their combination with the strong acid in the form of water. The substance H_2SO_4 can form a number of definite "hydrates" with water, and the combination is a very energetic one.

Dry Reactions.

On heating a sulphate on charcoal, in the reducing flame, together with pure sodium carbonate, sodium sulphide is formed, thus :

$$MgSO_4 + 2C + Na_2CO_3 = SNa_2 + MgO + 3CO_2.[\dagger]$$
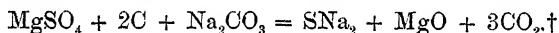
The fused mass when treated with an acid (HCl is best generally) gives off SH_2, readily recognised by its odour. When placed on a bright silver coin and moistened with a drop of acid it produces a black stain of silver sulphide. This reaction on charcoal with Na_2CO_3 applies, however, to all compounds containing sulphur.

Heated by themselves, the sulphates of the fixed alkalies and alkaline earthy metals, as well as of lead, are not decomposed. Acid sulphates ($HKSO_4$, &c.) are converted at a bright red heat into normal sulphates, with evolution of sulphuric acid. Other metallic sulphates become decomposed more or less speedily on ignition, giving off sulphuric or sulphurous anhydride and oxygen, according to the nature of the metal—*e.g.* :

$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2.$$
$$CuSO_4 = CuO + SO_2 + O.$$
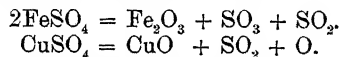
[*] Or NO_2HSO_3. As a matter of fact several compounds are contained in these white chamber crystals.

[†] In some cases a sulphide of the metal previously there as sulphate is produced, although much Na salt is present.

By distilling, in retorts, a mixture of ferrous and ferric sulphates an acid known as Nordhausen sulphuric acid is made. Its composition may be simplest represented as $H_2SO_4SO_3$. The action may be : $Fe_2(SO_4)_2(OH)_2 = Fe_2O_3 + H_2SO_4 + SO_3$. A definite compound can be obtained, on cooling, in crystals. On warming, however, SO_3 escapes.

Reactions in Solution.

A solution of potassium sulphate, K_2SO_4, or any soluble sulphate, may be employed.

Sulphuric acid forms normal and acid sulphates, which are mostly soluble in water, the exceptions being barium and lead sulphates, and a few basic sulphates, which, however, are soluble in acids.

$BaCl_2$ gives a white, finely divided precipitate of barium sulphate, $BaSO_4$, insoluble in dilute acids. Care must be taken not to have too much free hydrochloric or nitric acid present, lest any of their barium salts be precipitated, barium chloride and nitrate being much less soluble in concentrated acids than in water. If a very dilute solution of a sulphate has to be precipitated, the solution should be heated to boiling, and allowed to stand for some time after the addition of the barium salts.

This reaction distinguishes H_2SO_4 from all other acids except hydrofluosilicic acid, $2HF,SiF_4$, and selenic acid, H_2SeO_4, which are not by any means of common occurrence.

Soluble salts of strontium, calcium, and lead produce white precipitates of strontium, calcium, and lead sulphates, which are more or less soluble in large quantities of water : $CaSO_4$ being the most soluble, in about 500 parts of water, $SrSO_4$ dissolving in 7000 parts of cold water, and $PbSO_4$ in 22,000 parts of water only.

Since barium salts answer every purpose, recourse is rarely had to these reactions in order to detect sulphuric acid. The addition of alcohol (methylated spirit), ensures the complete precipitation of strontium, calcium, and lead sulphates. Most soluble sulphates can, in fact, be precipitated from their aqueous solutions by the addition of strong alcohol, in which they are insoluble.

In order to detect free sulphuric acid, the solution is evaporated to dryness on a water bath, together with a little cane sugar. A blackened or charred residue indicates free sulphuric acid, as no other acid is capable of decomposing cane sugar in like manner.

An insoluble sulphate can be decomposed by continued boiling with a concentrated solution of an alkali carbonate ; more readily by fusion with alkali carbonates (fusion mixture) into a soluble alkali sulphate, and an insoluble carbonate or oxide of the metal, thus :

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3.$$
$$PbSO_4 + Na_2CO_3 = Na_2SO_4 + PbO + CO_2.$$
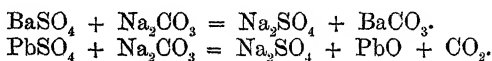
The fused mass is extracted with boiling water, and the insoluble carbonate or oxide separated by filtration from the solution of the alkali sulphate. The residue is examined as usual for bases, and the

solution for sulphuric acid, by acidulating with dilute hydrochloric acid (in order to destroy the excess of alkali carbonates), and adding barium chloride. Calcium sulphate dissolves in ammonium sulphate containing a little free ammonia ; lead sulphate in ammonium acetate or tartrate, or in sodium thiosulphate, or in strong HCl.

PERSULPHURIC ACID, $H_2S_2O_8$.—When sulphuric acid of 40 per cent. strength is electrolysed, the anhydride, S_2O_7, of persulphuric acid is produced. The acid itself has not been isolated. This anhydride decomposes on keeping, more rapidly on heating into SO_3 and oxygen.

Salts of persulphuric acid are produced in a similar manner. The solution must be kept cold, and the anode should be a platinum wire, as high density of current at the positive pole is required.

The persulphates are all soluble in water, those of potassium and barium being remarkable in this respect. $K_2S_2O_8$ is the most insoluble of the persulphates (1·77 in 100 water at 0°), whilst $BaS_2O_8.4H_2O$ is freely soluble.

The dry persulphates decompose on heating, forming the sulphate and liberating SO_3 and O_2. In solution, they slowly decompose. They are strong oxidising agents, oxidising ferrous salts readily, and from solutions of many metallic salts precipitate higher oxides.

Persulphates do not decolorise permanganate solutions, but slowly liberate iodine from KI.

Persulphates are used to some extent in analysis and for photographic purposes (reducing " contrasts " in negatives).

Tests.

$BaCl_2$ gives no precipitate with persulphates. On heating the dry salt and making a solution of the residue (except in the case of Ba and Pb), the addition of $BaCl_2$ gives a precipitate. $K_2Mn_2O_8$ is not decolorised (distinction from H_2O_2).

Chromium salts, as the sulphate or chrom-alum, are converted by a persulphate, in the presence of excess of an alkali hydroxide, into alkali chromates.

TiO_2 in strong H_2SO_4 gives no coloration (distinction from H_2O_2). A solution of a persulphate, made alkaline with NH_4HO, acts rapidly on zinc, cadmium, copper, and other metals.

SULPHUROUS ACID.—Obtained as a gaseous anhydride, SO_2, whenever sulphur is burnt in air or oxygen, or when metallic sulphides (pyrites, blende, galena, &c.) are roasted with free access of air ; also by the partial deoxidation of sulphuric acid by means of metals, such as Cu, Hg, Ag, or charcoal and various organic bodies, sulphur, &c. The gas is readily soluble in water, forming an acid solution, which combines with bases, and forms a series of salts, normal or acid, termed sulphites. They are characterised by the tendency they exhibit to absorb oxygen and become converted into sulphates.

xperiments (see also "Sulphur," *ante*).

SO_2 is very heavy, and can easily be collected in tubes by down-
ward displacement of air.

Prepare a few tubes of the gas by heating mercury or any other
metal (a few grams) with strong sulphuric acid in a small distilling
flask or test-tube, with cork and delivery tube.

I. In one introduce blue litmus paper ; it becomes red.

II. A burning taper is extinguished, and the gas does not in-
flame.

III. A piece of ignited magnesium ribbon continues to burn,
and some sulphur will be found amongst the MgO.

IV. A piece of filter paper moistened with permanganate will
become colourless, moistened with bichromate will become green.

Dry Reactions.

Sulphurous anhydride is recognised by its characteristic odour—
viz., that of burning sulphur. It combines readily with metallic per-
oxides, such as MnO_2, PbO_2, with formation of the corresponding
sulphates. In order, therefore, to remove SO_2 from a gaseous mixture,
the latter may be passed over PbO_2.

Most metallic sulphites are decomposed by heat into sulphates and
sulphides, thus : $4Na_2SO_3 = 3Na_2SO_4 + SNa_2$.

A few sulphites break up, on heating, into oxides and sulphur
dioxide.

Reactions in Solution.

A solution of sodium sulphite, Na_2SO_3, may be employed.

Sulphites are shown by the action of dilute sulphuric or hydro-
chloric acid upon them ; sulphurous anhydride, SO_2, is liberated, and
readily recognised by its pungent odour.

The only sulphites soluble in water are the alkali sulphites.
Normal barium, strontium, calcium, and magnesium sulphites, though
insoluble in water, are dissolved to a great extent by sulphurous acid,
with formation of acid sulphites, from which the normal salts are
reprecipitated on boiling. (See "Carbonates.") They are also soluble in
dilute hydrochloric acid (with decomposition) ; but on the addition of
an oxidising agent, such as chlorine water, free iodine, sodium hypo-
chlorite, nitric acid, &c., they are converted into sulphates, some of
which are insoluble.   (See "Sulphuric Acid.")

Commercial sulphites generally contain sulphates as impurities.
A precipitate consisting of barium sulphate is, therefore, frequently
obtained on adding barium chloride to an acidulated solution of a
soluble, or to a dilute hydrochloric acid solution of an insoluble,
sulphite.

On filtering off the precipitate, and adding chlorine water to
the filtrate, a further precipitate is obtained, showing the presence of
a sulphite.

Traces of sulphurous acid are distinguished with difficulty by

the odour alone, and it is preferable, therefore, to make use of the deoxidising as well as oxidising action which the acid can exert.

1. Sulphurous acid acts as a powerful reducing agent.

$AgNO_3$ gives with sodium sulphite a white precipitate of silver sulphite, Ag_2SO_3, soluble in excess of the alkali sulphite. The precipitate blackens on heating, owing to the separation of metallic silver, according to the equation : $Ag_2SO_3 + OH_2 = Ag_2 + H_2SO_4$.

$Hg_2(NO_3)_2$ produces a grey precipitate of metallic mercury, thus :

$$Na_2SO_3 + Hg_2(NO_3)_2 + H_2O = Na_2SO_4 + 2HNO_3 + 2Hg.$$
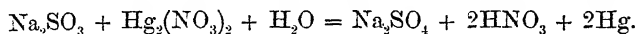
The instances of the reducing action of sulphurous acid are very numerous ; its action upon solutions of $AuCl_3$, H_2CrO_4, Fe_2Cl_6, and others, already noticed under the respective metals, need not be repeated here.

2. Under favourable circumstances sulphurous acid acts as an oxidising agent, especially when brought in contact with other more powerful reducing agents, such as nascent hydrogen, SH_2, $SnCl_2$, &c. Thus, by introducing the least trace of SO_2, or a sulphite, into a flask, in which hydrogen is generated from zinc and hydrochloric acid, SH_2 is immediately evolved, along with the hydrogen, and may be recognised by its odour and action upon lead paper. The change may be expressed as follows : $SO_2 + 3H_2 = SH_2 + 2OH_2$.

SO_2 and SH_2 give rise to the formation of pentathionic acid, with precipitation of white sulphur, according to the equation :

$$5SO_2 + 5SH_2 = H_2S_5O_6 + S_5 + 4OH_2.$$
$$\text{Pentathionic}$$
$$\text{acid.}$$
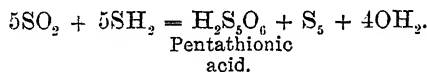
Sulphurous acid added to stannous chloride in the presence of hydrochloric acid gradually precipitates yellow SnS_2. The stannous chloride reduces the sulphurous acid, and the sulphuretted hydrogen and stannic chloride immediately react, with the production of SnS_2. The following equations express the changes :
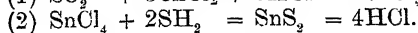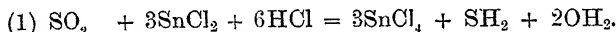
(1) $SO_2 + 3SnCl_2 + 6HCl = 3SnCl_4 + SH_2 + 2OH_2$.
(2) $SnCl_4 + 2SH_2 = SnS_2 = 4HCl$.
$$\text{Yellow}$$
$$\text{stannic sulphide.}$$

(See also " Phosphorus " and " Arsenic.")

An extremely delicate test for SO_2 is its decolorising action on a solution of permanganate. This should be only of the faintest pink tint ; the liberated gas is decanted into a test-tube and shaken with the permanganate.

THIOSULPHUROUS ACID (thiosulphuric acid).—This acid can only be kept for a short time in a free state in aqueous solution. Its sodium salt is an important compound, and may be obtained by

boiling a solution of sodium sulphite with sulphur,* or by the oxidation of sodium persulphide by contact with the air.

Dry Reactions.

All thiosulphates are decomposed on ignition. Alkali thiosulphates leave a polysulphide and a sulphate, thus :

$$4Na_2S_2O_3 = S_5Na_2 + 3Na_2SO_4.$$
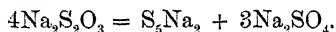
Some sulphur burns off if the heating take place in air.

### Reactions in Solution.

A solution of sodium thiosulphate ("hyposulphite"), $Na_2S_2O_3$, is the commonest and most easily soluble salt.

Most thiosulphates are soluble in water (barium thiosulphate is difficultly soluble in cold water), and their solutions may, with few exceptions, be boiled without decomposition. Calcium thiosulphate is gradually decomposed on boiling, the precipitate consisting of calcium sulphate and sulphur. When thiosulphates are treated with sulphuric or hydrochloric acid, sulphurous anhydride is evolved and sulphur is separated. The precipitated sulphur is yellow, and not white, as is usually the case when sulphur separates in chemical reactions. The change characterises thiosulphates.

The same instability of the sulphur atom, occupying the place of an atom of oxygen in sulphuric acid, is observed when thiosul-

* The action here is similar to that when a sulphide takes up O and becomes a sulphite, or when a sulphite takes up oxygen and forms a sulphate. The sulphur in thiosulphates is undoubtedly in two different states, which may be expressed by the formulæ :
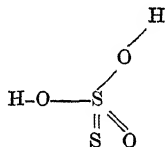
But it is also very probable that sulphites contain one hydroxyl, and the other hydrogen is directly attached to the sulphur :

    the other form being
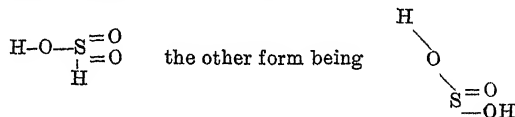
This sulphate may correspond to the formula given under sulphuric acid ;
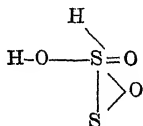
but, as before stated, proof is wanting to decide which is most likely.

phates come in contact with salts whose metals form insoluble sulphides.

$AgNO_3$ gives a white precipitate of silver thiosulphate, $Ag_2S_2O_3$, soluble in sodium thiosulphate, which speedily turns yellow, then brown, and lastly black (SAg_2), especially on the application of heat, thus: $Ag_2S_2O_3 + OH_2 = SAg_2 + H_2SO_4$.

Mercurous nitrate and lead acetate give similar precipitates, which are decomposed by heat into Hg_2S or PbS, and sulphuric acid.

$SnCl_2$ gives a brown precipitate of SnS.

Thiosulphates, like sulphites, are readily oxidised, but yield, under certain conditions, oxygen to more powerful reducing agents, and thus become oxidising agents.

Free chlorine, sodium hypochlorite, ferric chloride, &c., oxidise thiosulphates in the presence of water completely to sulphates, even when cold, thus:

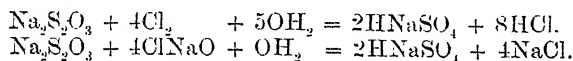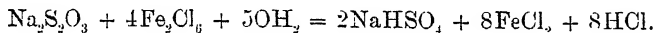$$Na_2S_2O_3 + 4Cl_2 \quad + 5OH_2 = 2HNaSO_4 + 8HCl.$$
$$Na_2S_2O_3 + 4ClNaO + OH_2 \quad = 2HNaSO_4 + 4NaCl.$$

$Na_2S_2O_3$ gives with Fe_2Cl_6 at first a reddish violet coloration (difference between sulphites and thiosulphates), but on standing the solution is slowly decolorised (more readily on heating), with formation of $FeCl_2$, thus:

$$Na_2S_2O_3 + 4Fe_2Cl_6 + 5OH_2 = 2NaHSO_4 + 8FeCl_2 + 8HCl.$$

Nascent hydrogen reduces thiosulphates, and sulphuretted hydrogen is evolved:

$$Na_2S_2O_3 + 4H_2 + 2HCl = 2SH_2 + 3OH_2 + 2NaCl.$$

Some sulphur is always precipitated as well.

Sodium thiosulphate is a useful solvent for haloid silver salts (for which it is much used in photography), Hg_2Cl_2 and $PbSO_4$. Calcium thiosulphate, CaS_2O_3, is used as an agent for removing the last traces of chlorine in the bleaching of paper pulp, and from fabrics bleached by means of bleaching powder, to prevent their deterioration by the traces of chlorine which they are apt to retain. It has on that account received the name of "antichlor." The free hydrochloric acid which is formed in the reaction is neutralised by passing the fabrics through a weak alkali bath. Sulphites are also used for this purpose.

The property of sodium thiosulphate of dissolving AgCl has found an important metallurgical application in the removal of silver from poor argentiferous ores, after they have undergone the process of roasting with common salt, which converts the silver into AgCl, insoluble in water.

A still lower oxide of sulphur, SO or S_2O_2, the hydrate of which is probably H_2SO_2, is obtained in combination when metallic zinc is placed in a solution of SO_2 in water. No gas is evolved at first, but the solution becomes coloured brown, a zinc salt, which rapidly

decomposes, being formed. Very little is known with certainty about the compounds so produced. Metallic zinc dissolves also in hydrogen sodium sulphite; the reaction may be :

$$2(NaHSO_3) + Zn = \underbrace{H_2O + Na_2ZnS_2O_4}.$$
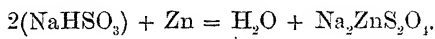
It is a very powerful reducing agent, precipitating the metal from salts of copper or lead, bleaching indigo and other colouring-matters, &c.

HYDROSULPHURIC ACID (sulphuretted hydrogen), SH_2, is obtained as a colourless gas by the decomposition of certain metallic sulphides, such as FeS, ZnS, Sb_2S_3, by means of sulphuric or hydrochloric acid. It is characterised by a fœtid odour, resembling that of rotten eggs. It is absorbed by cold water, forming sulphuretted hydrogen water, which reddens blue litmus paper feebly. Hydrosulphuric acid exchanges its sulphur for the oxygen of most metallic oxides, forming water and metallic sulphides, and is on this account a most valuable reagent. Many native sulphides—e.g., iron pyrites, galena, cinnabar, zinc blende—are met with in vast masses, and constitute the principal minerals from which the metals are extracted.

Dry Reactions.

Metallic sulphides are acted upon in various ways when submitted to heat. Some are decomposed, when heated in a close vessel, into metal and sulphur—e.g., Au_2S_3; some sulphides, such as PtS_2, FeS_2, Sb_2S_5, SnS_2, PbS, yield up a portion of their sulphur, and are reduced to PtS, Fe_3S_4 or FeS, Sb_2S_3, SnS, Pb_2S; others sublime without decomposition, such as As_2S_3 (orpiment), HgS (cinnabar). A great number of metallic sulphides remain, however, undecomposed, when heated out of contact with atmospheric air.

Most sulphides undergo a change when roasted in a tube open at both ends. SAg_2 leaves metallic silver (usually also a little Ag_2SO_4); the sulphur, combining with oxygen, passes off as SO_2. Some sulphides leave a metallic oxide—e.g., SnS, Sb_2S_3, Bi_2S_3; others, again, such as the sulphides of the alkalies and alkaline earthy metals, are converted into sulphates. Lead sulphide (galena) is converted into a mixture of oxide and sulphate; cupric sulphide, when roasted at a high temperature, yields SO_2 and CuO, at a lower temperature $CuSO_4$. FeS and other sulphides of the iron group are partially converted into sulphates, which, on the application of a stronger heat, lose their acid, leaving metallic oxides. Many native metallic sulphides are distinguished for their metallic lustre, such as iron and copper pyrites, galena, grey antimony, &c.

Reactions in Solution.

Alkali and alkaline earthy sulphides are soluble in water (CaS and MgS are only sparingly soluble). Dilute hydrochloric acid decomposes them readily into metallic chlorides and SH_2. All other sulphides are insoluble in water. FeS, MnS, ZnS are decomposed

by dilute hydrochloric acid, with evolution of sulphuretted hydrogen. Others require concentrated hydrochloric acid, such as NiS, CoS, Sb_2S_3, SnS_2, PbS. The rapidity of the action of acids on sulphides depends very much on the physical state of the latter. Sulphides which are insoluble, or difficultly soluble, in concentrated hydrochloric acid, such as Bi_2S_3, CuS, SAg_2, PbS, As_2S_3, are decomposed by concentrated nitric acid; they are generally oxidised into sulphates—at first with separation of sulphur, which by prolonged digestion is for the most part converted into sulphuric acid. Others, such as HgS, PtS_2, Au_2S_3 (As_2S_3), dissolve easily only in aqua regia, or hydrochloric acid and potassium chlorate, with separation of sulphur and formation of sulphuric acid, and of a metallic chloride. On dissolving PbS, SnS_2, Sb_2S_3, As_2S_3 in concentrated nitric instead of hydrochloric acid, they are converted principally into $PbSO_4$, SnO_2, Sb_2O_4, H_3AsO_4.

To detect SH_2 (in an aqueous solution) or a soluble sulphide (a solution of ammonium sulphide may be conveniently employed for illustration), add a solution of a salt of cadmium, lead, or silver, which gives by double decomposition a characteristic precipitate of a metallic sulphide—fine yellow for cadmium, black for lead or silver salts.

To examine a sulphide decomposable by hydrochloric acid, the evolved sulphuretted hydrogen gas is made to act upon lead paper or is passed through a solution of a lead salt. (Iron pyrites and copper pyrites give off SH_2 in the presence of zinc only.)

Sulphides which are not decomposed by hydrochloric acid yield sulphur on treatment with nitric acid or aqua regia, and must be recognised by this and the products of decomposition, such as SnO_2, $PbSO_4$, as well as the reactions which they give when examined in the dry way.

Many native sulphides, such as fahl ore, &c., are expeditiously examined by heating the finely powdered mineral in a hard glass tube, in a current of dry chlorine gas, when the metals are converted into chlorides and the sulphur into volatile chloride of sulphur, which is decomposed on being passed into water, HCl, H_2SO_4, and S resulting.

To detect a soluble alkali sulphide in the presence of free SH_2, add a few drops of a solution of sodium nitroprusside. This reagent does not affect free SH_2, but gives a fine purple colour with the merest traces of soluble sulphides. The colour disappears only after some time. It does not show in the presence of free alkali hydroxides.*

A mixture containing a soluble sulphide, thiosulphate, sulphite, or sulphate may be examined by adding cadmium carbonate, $CdCO_3$, to the aqueous solution. Filter after agitation, dissolve the excess of

* Sodium nitroprusside, $Fe(CN)_4NOCNNa_2$, may be readily prepared by heating a few crystals of potassium ferricyanide with concentrated nitric acid in a test-tube until red fumes are copiously evolved, then diluting with water, and neutralising with sodium carbonate. The solution may be used directly for testing for sulphides. (Playfair.)

$CdCO_3$ in the precipitate by means of dilute acetic acid ; a residue of yellow CdS indicates the presence of a sulphide. Add $BaCl_2$ to the filtrate ; a precipitate is obtained consisting of $BaSO_4$ and $BaSO_3$. Filter off ; digest the precipitate with dilute hydrochloric acid, and filter. A white residue shows the presence of a sulphate. Add chlorine water to the filtrate ; a precipitate of $BaSO_4$ indicates the presence of a sulphite. The filtrate from the $BaCl_2$ precipitate is examined for thiosulphates by the addition of HCl and boiling. A precipitate of yellow sulphur and the odour of SO_2 indicate the presence of a thiosulphate.

To remove SH_2 from a gaseous mixture of CO_2 and SH_2, shake up a solution of cupric or cadmium chloride with the gases.

Experiments.

SH_2 being heavier than air, can be collected in tubes by downward displacement. The most convenient mode of preparation is by acting on FeS with HCl. It can be done in a flask or tube, with delivery tube. Aluminium sulphide is also convenient, as it is decomposed by water.

I. Blue litmus paper, when moist, is reddened.

II. A taper is extinguished, but the gas burns, forming water, which will make a deposit of moisture on a cold substance, and a little SO_2 and some sulphur will be deposited on the sides of the tube as the flame sinks.

III. A piece of paper moistened with lead acetate is turned black on immersion in the gas ; a silver coin placed on the top of the tube will also be blackened.

NITRIC ACID, HNO_3, is obtained as a colourless, highly corrosive distillate when nitrates are gently heated with strong sulphuric acid, and the vapour which arises condensed. It is characterised by the facility with which it parts with its oxygen, and it is on this property that the detection of nitric acid or a nitrate depends. Crude nitric acid is yellow, because of partial decomposition into nitrous acid, and presence of oxides of nitrogen.

Dry Reactions and Experiments.

Most nitrates fuse readily when heated. All are decomposed when heated to a high temperature. The decomposition products vary with the nature of the base, and to some extent with the temperature employed, an oxide of nitrogen and oxygen generally being given off. Thus, ammonium nitrate, NH_4NO_3, breaks up into ON_2 and $2(OH_2)$; potassium or sodium nitrate into nitrite (always contaminated, however, with nitrate and oxide), with liberation of oxygen, and ultimately, on the application of a stronger heat, into oxide or peroxide—nitrogen and oxygen being given off ; others, such as lead nitrate, into O and N_2O_4, leaving the oxide of the metal. When heated together with substances capable of taking up oxygen, such as carbon, charcoal, alkali cyanides, sulphur, or phosphorus, the

decomposition becomes explosively violent, and free nitrogen gas only is liberated. (Chlorates explode in like manner, but leave metallic chlorides.)

Reactions in Solution.

With the exception of a few basic salts, nitrates are readily soluble in water; hence nitric acid cannot be detected in the usual way— that is, by producing precipitates by double decomposition. When acted upon by reducing agents, *e.g.*, nascent H, the deoxidation of the acid may be partial, to some of the lower oxides of nitrogen, or complete to nitrogen, or to ammonia or hydroxylamine.

Quite a number of intermediate products can be obtained from the action of nascent hydrogen on nitrates.

$$N_2O_4 \text{ or } NO_2$$
$$N_2O_3$$
$$N_2O_2 \text{ or } NO$$
$$N_2O$$
$$NH_2OH$$
$$NH_3.$$
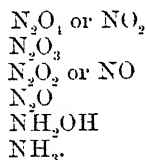
1st. Reactions in which nitric acid is reduced to oxides of nitrogen.

Dilute nitric acid, or a solution of potassium nitrate, KNO_3, may be employed.

Nitric acid and nitrates are decomposed when heated with concentrated hydrochloric acid (or a chloride when heated with nitric acid). Nitrosyl chloride, $NOCl$, and chlorine are evolved, and the liquid acquires the power of dissolving gold leaf or platinum foil (see these metals) because of the chlorine produced. (Chlorates, bromates, iodates, chromates, and permanganates also evolve chlorine when treated with hydrochloric acid.)

Pour some concentrated sulphuric acid (free from nitric acid) upon a little potassium nitrate, in a dry test-tube, see that the mixture is cool, and then add gradually a solution of ferrous sulphate so that it lies upon the sulphuric acid—not mixing with it—or, better, a few crystals of ferrous sulphate. A ring is seen to form at the point of contact of the two layers, or around the crystals, of a violet-red or dark brown colour, according to the quantity of the nitrate present. The coloration is increased by *very slight* agitation, but it disappears on heating. This is owing to the formation of a transient compound of the ferrous salt with N_2O_2 ($4FeSO_4,N_2O_2$). The other three atoms of oxygen from two molecules of nitric acid oxidise six molecules of ferrous into three molecules of ferric sulphate, $Fe_2(SO_4)_3$. This is the usual method by which nitric acid is detected. The change may be expressed thus :

$$10FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4FeSO_4,N_2O_2 + 4OH_2.$$
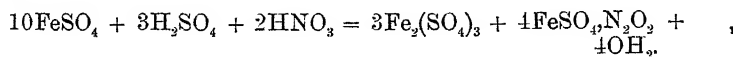
A solution of a nitrate, when added to a hot solution of indigo

in sulphuric acid (sulphindigotic acid), changes the blue colour of
the indigo to yellow.   (Free chlorine and other oxidising agents also
bleach indigo.)

Metals, Cu, Ag, Zn, Pb, or Hg, are dissolved by nitric acid, with ·
evolution of ruddy fumes, and also by a mixture of a nitrate with
strong sulphuric acid.   A similar reaction takes place when copper
filings are mixed with a nitrate and hydrogen potassium sulphate
and fused in a test-tube or crucible.

**2nd. Reactions in which nitric acid is entirely reduced,
and its nitrogen converted into ammonia.**

All nitrates when fused with caustic alkalies, lime, or soda-lime,
and some non-nitrogenous organic substance, such as sugar or starch,
evolve ammonia.

The gas may be readily recognised by its odour, or action upon
red litmus paper.   The experiment may be done in a test-tube.

Nascent hydrogen, produced by the action of KHO upon metallic
zinc, iron, or aluminium, gives rise, in the presence of a nitrate, to
the formation of ammonia, thus :

(1) $Zn + 2KHO = Zn(KO)_2 + H_2$.
(2) $KNO_3 + 4H_2 = NH_3 + KHO$ * $+ 2OH_2$.
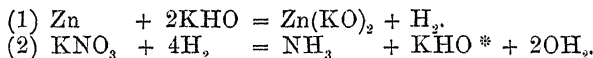
When stannous chloride, hydrochloric acid, and a nitrate are
heated together, the tendency of the stannous chloride to combine
with two more atoms of chlorine to form stannic chloride, aided by
the oxidising action of nitric acid upon the hydrogen, breaks up
hydrochloric acid, with formation of stannic chloride and ammonia,
thus :

$4SnCl_2 + KNO_3 + 10HCl = 4SnCl_4 + NH_4Cl + KCl + 3OH_2$.
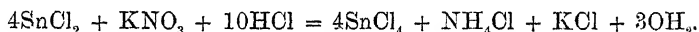
Nitrates gently heated together with ammonium salts, as KNO_3
and NH_4Cl, give nitrous oxide as one product :

$KNO_3 + NH_4Cl = KCl + H_2O + N_2O$.
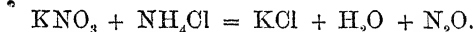
N_2O supports the burning of a glowing match.

To detect free nitric acid in the presence of a nitrate, evaporate
the solution on a water-bath with quill cuttings or white wool or
silk.   Nitric acid colours these substances yellow.

Ammonium nitrate and the nitrates of other amines behave in a
somewhat peculiar manner with metals and some benzenic com-
pounds.

NITROUS ACID, HNO_2.—Both the acid and anhydride are marked
by their proneness to undergo decomposition, in the presence of
water, into nitric acid and nitric oxide.

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* The KHO represented here is in practice further changed by the metal
employed.

Dry Reactions.

Nitrites fuse and are decomposed on ignition into oxides, with evolution of nitrogen and oxygen. Mixed with carbon, potassium cyanide, sulphur, and other oxidisable bodies, nitrites deflagrate like nitrates, with which they have, in fact, most of the dry reactions in common.

Reactions in Solution.

All nitrites are soluble in water; silver nitrite, $AgNO_2$, although readily soluble in hot water, is somewhat difficultly soluble in cold water (300 parts), and serves for the preparation of pure nitrites, by double decomposition with neutral soluble chlorides. Dilute acids liberate N_2O_3 and convert a portion of the nitrite into nitrate, thus: $3KNO_2 + H_2SO_4 = N_2O_3 + KNO_3 + K_2SO_4 + OH_2$.*

The reactions by which the presence of nitrous acid can be readily recognised may be divided into two classes:

1st. Reactions in which the acid acts as an oxidising agent.

SH_2 decomposes aqueous solutions of alkali nitrites, with formation of N_2O_2 (of NH_3 when the reaction goes on for some time) and alkali sulphides, thus:

$$2KNO_2 + 2SH_2 = N_2O_2 + 2OH_2 + S_2K_2.$$
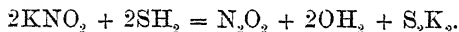
In acid solutions the decomposition is accompanied by a copious separation of sulphur.

Acid solutions of ferrous salts are turned dark brown on addition of a nitrite, owing to the absorption of N_2O_2 gas by a portion of the unoxidised ferrous salt. On the application of heat N_2O_2 is evolved, thus:

$$2FeCl_2 + 4HCl + 2KNO_2 = Fe_2Cl_6 + 2KCl + N_2O_2 + 2OH_2.$$
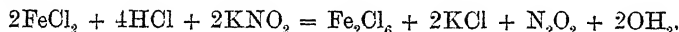
Ammonium nitrite, $NO_2(NH_4)$, breaks up on the application of heat into N and OH_2. Nitrites containing fixed bases are decomposed in like manner on the addition of an ammonium salt, thus:

$$(NH_4)_2CO_3 + 2KNO_2 = N_4 + 4OH_2 + K_2CO_3.$$
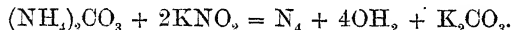
KI and starch solution give in the presence of a nitrite and a dilute acid blue iodide of starch. (See also HI.)

When a very dilute solution of a nitrite—say a polluted well water—is added to a cold saturated solution of sulphate of diamido-benzoic acid and the nitrous acid liberated with a few drops of dilute acid (H_2SO_4), the solution acquires an intense yellow colour. As little as $\frac{1}{5}$ mgr. of N_2O_3 diffused in one litre of water can thus readily be discovered. Diphenylamine dissolved in an acid, as HCl, gives a blue colour with a minute quantity of nitrous acid. The HCl compound of phenylenediamine is even more delicate in its indication, a rosy colour being produced. Possibly the most delicate

* As performed in the usual way, red fumes are always produced, due to formation of N_2O_3 and NO_2 by contact of the N_2O_2 with air.

test for nitrous acid is a mixture of α-naphtylamine and sulphanilic acid dissolved in a slight excess of H_2SO_4. Exceedingly minute quantities of HNO_2 give with this reagent a lovely rosy red coloration, due to the formation of a diazo derivative.

 $= \alpha$-naphtylamine $= C_{10}H_7NH_2$.

 $=$ sulphanilic acid $= C_6H_4NH_2SO_3H$.
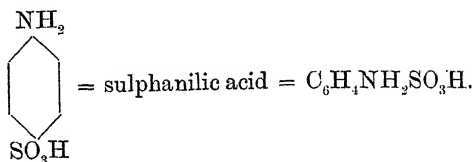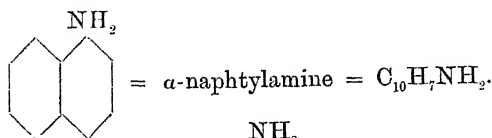
The reagent should be made by dissolving equivalent weights of α-naphtylamine and sulphanilic acid in moderately strong H_2SO_4. This solution should be colourless. A few drops only of the solution to be tested is diluted with twenty to fifty times as much water and one cubic centimetre of the α-naphtylamine solution added. A rosy pink colour should appear within ten minutes.

The test is somewhat too delicate for most ordinary purposes.

2nd. Reactions in which the acid acts as a reducing agent, and is converted into nitric acid, thus:

$$2HNO_2 + O_2 = 2HNO_3.$$
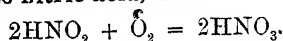
$AuCl_3$ and Hg_2Cl_2 give metallic gold and grey metallic mercury respectively.

$K_2Mn_2O_8$ oxidises nitrites into nitrates in the presence of a mineral acid (H_2SO_4), and the permanganate solution is rapidly decolorised, especially if the solution be warmed.

Potassium dichromate is reduced under similar conditions to a green salt of chromium. Nitrates are not affected by potassium permanganate or alkali chromates.

PbO_2 converts HNO_2 into HNO_3, but does not act upon very dilute HNO_3.

Hydroxylamine, NH_2OH, is formed in many processes of reduction of oxides of nitrogen as a preliminary to the formation of ammonia. Tin and nitric acid produce a little, the hydrogen displaced from the acid by the tin reacting thus:

$$HNO_3 + 3H_2 = NH_2OH + 2H_2O.$$
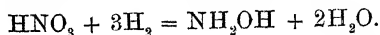
Salts are known, as NH_2OHHCl and NH_2OHHNO_3, but they are somewhat unstable, and the free base more so. Cupric salts are reduced, in alkaline solutions, to cuprous oxide (characteristic reaction), and mercuric salts to mercurous.

Hydrazine, N_2H_4, can be looked upon as diamidogen, $\genfrac{}{}{0pt}{}{NH_2}{NH_2}$, the

semi-molecule, NH_2, of which was supposed to exist in combination in amides. The substance may be obtained by several "organic" reactions, and also by the action of sodium amalgam on an aqueous solution of potassium nitrosyl sulphate, $K_2SO_3N_2O_3$. This substance is formed when sulphur dioxide is passed into a solution of potassium nitrite. N_2H_4 is gaseous, but dissolves in and forms a compound with water, $N_2H_4H_2O$, which boils at 118·5°. The anhydrous compound boils at 113°. It forms salts with acids, as N_2H_4HCl, $N_2H_4 2HCl$, and $N_2H_4H_2SO_4$. This sulphate is one of the least soluble of the hydrazine salts. The base itself has a powerful reducing action on salts of Cu, Ag, Hg, &c., at ordinary temperatures. Platinum and gold solutions are immediately reduced.

Hydrazoic acid, $\overset{N}{\underset{N}{>}}NH$, was first obtained from organic compound of hydrazine. It can be obtained as a sodium salt by the action of N_2O on sodium amide, NH_2Na.

$$2NaNH_2 + N_2O = NaN_3 + NaOH + NH_3.$$

This mode of preparation is dangerous.

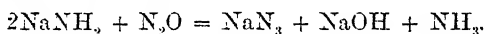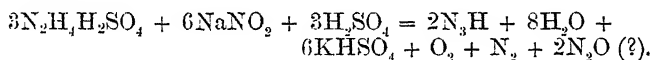Hydrazine sulphate and nitrous acid react, analogously to the diazo reaction, thus :

$$3N_2H_4H_2SO_4 + 6NaNO_2 + 3H_2SO_4 = 2N_3H + 8H_2O + \\ 6KHSO_4 + O_2 + N_2 + 2N_2O \text{ (?)}.$$

The pure substance is a very volatile and evil-smelling liquid, which boils at 37°, and is most highly explosive either as liquid, vapour, or in solution. Its solution is acid, and dissolves zinc and other metals, giving crystalline salts, which also explode most violently when heated.

The ammonium salt has the composition N_3HNH_3. It is a white crystalline compound which flashes off on contact with a flame, and detonates on percussion or heating in a closed vessel. It is probably the most powerful explosive at present known. The silver salt, AgN_3, is formed as a white, very insoluble precipitate on addition of a solution of hydrazoic acid to any soluble silver salt. It closely resembles silver chloride in appearance. On heating or percussion it explodes with extreme violence.

HYDROCHLORIC ACID.—Hydrogen chloride, HCl, is readily absorbed by water, and forms one of the most useful acids. Chlorides are an important class of chemical compounds, and are very widely distributed in nature.

Some chlorides are liquid at the ordinary temperature, and can be distilled without decomposition, such as $SnCl_4$, PCl_3, and CCl_4; $SbCl_3$ is a soft, white, crystalline solid which distils at 225° C.; others are solid, but fusible at moderately high temperatures, but not very volatile until heated to temperatures such as the melting-points of copper or platinum.

Most chlorides *seem* to be more volatile in a current of air, but some decomposition always occurs.

Experiments (see *ante*).

I. HCl is given off as a gas when a chloride is treated with strong H_2SO_4. NaCl, sodium chloride, is the substance used for the source of chlorine, hydrochloric acid, and of sodium compounds. Arrange a large test-tube or flask with delivery tube, charge with common salt, and drop on to this strong H_2SO_4. The gas will escape and be nearly dry. $NaCl + H_2SO_4 = NaHSO_4 + HCl$. It is not necessary to heat the substances. Several dry tubes may be filled by the gas by downward displacement, and then covered with a waxed plate.

N.B.—The most convenient covering for a test-tube in which a gas has been collected is a watch-glass in which some paraffin wax has been melted and allowed to become almost solid, and the wax then gently pressed on the top of the test-tube.
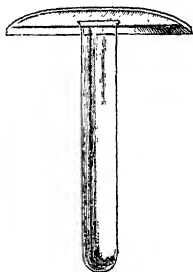
Place in the tube a piece of well dried blue litmus; notice the colour hardly changes until moisture has been absorbed; also notice the white fumes when the gas comes in contact with moist air.

II. Introduce a burning taper. It is extinguished and the gas does not ignite or burn.

III. Pour in lime water; remains clear.

IV. Introduce quickly into a tube of the dry gas a little zinc or magnesium filings or aluminium foil, shake up for a minute, holding the waxed cover tightly on, and then test the gas in the tube with a flame.

FIG. 92.

It should burn with a flame like hydrogen, because:

$$Mg + 2HCl = H_2 + MgCl_2.$$
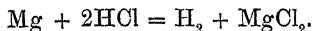
V. A tube of the gas should be inverted with the mouth under cold water, and then the cover removed; water should enter the tube, almost filling it. Litmus placed in this water is reddened.

VI. A gram or so of MnO_2, or $K_2Mn_2O_8$, or PbO_2, in powder, dropped into a tube of HCl, liberates a little chlorine. After standing a minute or so a piece of blue litmus should be bleached on placing in the gas.

Reactions.

Upon ignition certain chlorides, such as $AuCl_3$, $PtCl_4$, are decomposed, with evolution of chlorine gas, first into AuCl and $PtCl_2$, which are almost insoluble in water, and finally into Au and Pt. Magnesium chloride is decomposed by heat in the presence of water into oxychloride, with formation of HCl. Anhydrous ferric chloride, when heated in contact with air, is decomposed into Fe_2O_3 and $3Cl_2$. Similarly with aluminic chloride, which also decomposes very energetically with water and substances containing hydroxyl, or with certain hydrocarbons and halogen compounds.

Heated in a bead of microcosmic salt saturated with cupric oxide, chlorides impart a blue colour to the outer flame, owing to the formation of volatile $CuCl_2$.

When a dry chloride is mixed with potassium dichromate and concentrated sulphuric acid, and gently heated, a deep brownish red gas, called chlorochromic acid or chromylic chloride, CrO_2Cl_2, is formed, and can be collected in a receiver. It is a deep red, almost black liquid. The reaction taking place is expressed by the equation :

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 = 2CrO_2Cl_2 + 2Na_2SO_4 +$$

Chlorochromic acid
or chromyl-chloride.

$$K_2SO_4 + 3OH_2.$$
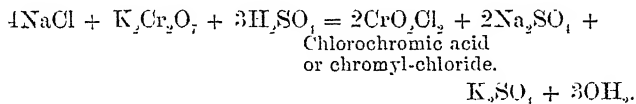
This liquid is decomposed, on mixing with water, into chromic and hydrochloric acids, thus : $CrO_2Cl_2 + 2OH_2 = H_2CrO_4 + 2HCl$; or by aqueous ammonia or potassium hydroxide into the corresponding salts. The presence of chromic acid, and *indirectly* of hydrochloric acid, is inferred from the yellow precipitate which a lead salt produces with these solutions.

The reaction may be employed for recognising a chloride in the presence of a bromide or iodide. The two latter are liberated as Br and I respectively, and on the addition of sodium or potassium hydroxides are dissolved to a colourless solution.

To make sure in case of a mixture it is better to test for Cr in the aqueous solution of the distillate either by the hydrogen-peroxide reaction or with a bead of sodium carbonate. (See " Chromic Acid.")

Chlorides may be divided into :

1st. Chlorides insoluble in water, such as AgCl and Hg_2Cl_2, which are quite insoluble; $PbCl_2$, soluble in 135 parts of cold water, readily soluble in boiling water ; and Cu_2Cl_2, almost insoluble in water, also in dilute sulphuric acid ; soluble in ammonium hydroxide, HCl and NaCl solutions. AuCl and $PtCl_2$ are almost insoluble in water, but form soluble double salts with a number of other chlorides.

2nd. Chlorides which are soluble in water, comprising most other chlorides. The chlorides of the more positive metals, as K, Na, Ba, &c., are less soluble in aqueous HCl and strong acid solutions than in OH_2.

Some chlorides of the less positive elements (with the exception of Hg and Ag) are decomposed by water, with formation of free acid and metallic oxides or hydroxides, *e.g.*, $AsCl_3$ (forms As_2O_3), or of some insoluble oxychloride ($SbCl_3$ gives SbOCl ; $BiCl_3$ gives BiOCl); soluble, however, in excess of HCl.

$AgNO_3$ gives a white curdy precipitate of silver chloride, AgCl, the formation of which is not affected by the presence of dilute or even moderately strong nitric acid. The precipitate turns violet on exposure to light. It is insoluble in nitric acid ; soluble in ammonium hydroxide, but is reprecipitated therefrom unchanged on the addition

of nitric acid ; it is likewise soluble in potassium cyanide and sodium thiosulphate, and to a considerable extent in hydrochloric acid, and alkali chlorides (especially LiCl, from which it is reprecipitated on dilution). Silver chloride fuses when heated nearly to redness without undergoing decomposition, to a transparent horn-like mass, called horn-silver.

Chlorides are decomposed on heating with manganic oxide and concentrated sulphuric acid, when chlorine is evolved, according to the equation :

$$MnO_2 + 2NaCl + 2H_2SO_4 = Cl_2 + MnSO_4 + Na_2SO_4 + 2OH_2.$$
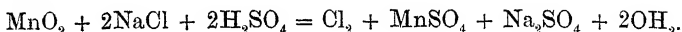
This gas is readily recognised by its bleaching properties, its yellowish green colour, and its action upon iodised starch paper, or upon a dilute solution of potassium iodide and freshly prepared starch solution, giving rise to the formation of blue iodide of starch.

Concentrated sulphuric acid liberates gaseous hydrochloric acid from chlorides.

$HgCl_2$, Hg_2Cl_2, $AgCl$, $PbCl_2$, $SnCl_2$, and $SnCl_4$ are decomposed with some difficulty, or very slowly, by concentrated sulphuric acid. Potassium hydrogen sulphate fused with these chlorides liberates HCl. Traces of free HCl in the presence of a soluble chloride are best detected by gently heating with MnO_2 or PbO_2, and passing the evolved chlorine into a solution of potassium iodide and starch. The chlorine liberates iodine $(2KI + Cl_2 = 2KCl + I_2)$, which gives a blue colour with the starch.

CHLORIC ACID, $HClO_3$.—Is obtained in combination with calcium, by passing chlorine through a hot solution of calcium hydroxide to complete saturation :

$$6Ca(HO)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6OH_2.$$
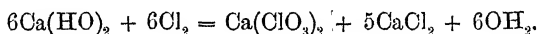
By adding KCl to the solution calcium chloride and potassium chlorate, $KClO_3$, are formed by double decomposition. Potassium chlorate, being little soluble in cold water, and still less so in a solution of calcium chloride, crystallises out, and is washed with cold water and purified by recrystallisation.

Free chloric acid, $HClO_3$, cannot be kept in a free state for very long. Even at the ordinary temperature it undergoes decomposition, generally explosively. It can be obtained in solution by adding the exact amount of H_2SO_4, dilute, to a cold solution of barium chlorate. On evaporating at a low temperature in a vacuum it may be concentrated, but the operation is too dangerous for any ordinary workers.

Dry Reactions of Chlorates.

All chlorates are decomposed by heat; they fuse and evolve oxygen, or a mixture of chlorine and oxygen, according to the greater

or less affinity of the metal for oxygen or chlorine, leaving a residue, consisting of a metallic chloride, oxychloride, or oxide.*

On heating a few crystals of potassium chlorate in a test-tube, the presence of oxygen can be shown by introducing a glowing splinter of wood into the test-tube. On dissolving the fused mass in water, and adding a drop of silver nitrate, a white, curdy precipitate is obtained, whilst a solution of a chlorate (unignited) gives no, or only a very slight, precipitate.

Chlorates part with their oxygen far more readily, when heated, than nitrates. When mixed with oxidisable substances, such as C, S, P, cyanides, or sulphides, they explode violently when gently rubbed together in a mortar, or when moistened with a drop of concentrated sulphuric acid. Care must therefore be taken not to powder, or heat together, a chlorate with organic substances, even in small quantity, and especially not with sulphur or sulphides or phosphorus. Chlorates and red phosphorus explode, or ignite, when very gently rubbed together on paper. Matches and many igniting compositions for military purposes depend on these properties for their action. Chlorates and finely divided metals, as aluminium powder, magnesium filings, &c., are employed to produce flashlights for photographic purposes. These mixtures are very dangerous, as they explode on percussion as well as by contact with a flame.

Experiments and Reactions in Solution.

A solution of potassium chlorate may be employed.

All chlorates are soluble in water.

Concentrated sulphuric acid decomposes potassium chlorate at quite a low temperature, a reddish liquid and greenish yellow gas, called chloric peroxide, Cl_2O_4, being formed, which is recognised by its suffocating odour. On the application of heat a violent explosion occurs, due to the resolution of Cl_2O_4 into chlorine and oxygen. A single crystal only of the chlorate should be employed, and the test-tube should be held with its mouth turned away from the operator. The change may possibly be expressed by the equations :

$$2KClO_3 + H_2SO_4 = K_2SO_4 + 2HClO_3 ;$$
$$4(HClO_3) = 2H_2O + 2(Cl_2O_4) + O_2.$$
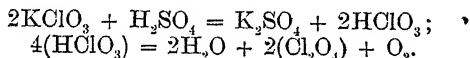
A chlorate dropped into *hot* sulphuric acid gives off a mixture of chlorine and oxygen gases. This is quite safe.

Strong hydrochloric acid, especially when heated, decomposes potassium chlorate, giving off a mixture of chloric peroxide and free chlorine, thus :

$$8KClO_3 + 24HCl = 6ClO_2 + 9Cl_2 + 8KCl + 12OH_2.$$
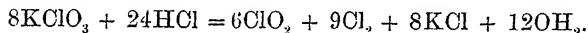
* Some metallic oxides aid the decomposition of chlorates very considerably when mixed with them and gently heated. This is the case with MnO_2. A little Cl is liberated and a corresponding amount of K_2MnO_4 formed. This decomposes at about 240°, and the MnO_2 and K_2O resulting act on the $KClO_3$, reforming K_2MnO_4, to undergo the same cycle of changes. Other oxides, especially those of the more negative elements, turn out both oxygen and chlorine—*e.g.*, WO_3, SnO_2, TiO_2, $(UO)_2O_3$, MoO_3, &c.

A solution of indigo (sulphindigotic acid) is decolorised on the addition of a chlorate and dilute sulphuric acid, by a reaction analogous to that produced by free nitric acid.

Sulphur dioxide, as gas, on contact with a solid chlorate becomes oxidised, a white cloud of SO_3 and a greenish gas, ClO_2, being produced. The chlorate is eventually converted into sulphate.

An aqueous solution of a chlorate behaves in a similar manner towards sulphurous acid, but no ClO_2 is liberated.

PERCHLORIC ACID, $HClO_4$.—Perchlorates are more stable than chlorates. Concentrated sulphuric acid fails to decompose them when cold, and with difficulty only on heating. (Distinction from chlorates.) Hydrochloric, nitric, and sulphurous acids do not decompose aqueous solutions of perchlorates, nor is indigo solution decolorised. All perchlorates are soluble in water, most of them freely. Potassium perchlorate is sparingly soluble in cold water, and insoluble in alcohol.

A certain quantity of potassium perchlorate, $KClO_4$, is formed when potassium chlorate is heated to a moderate temperature, until *some* oxygen has been given off. The residue then contains a mixture of chlorate, chloride, and perchlorate. The equation $2KClO_3 = KCl + KClO_4 + O_2$ has been proposed, but disputed on experimental grounds. Possibly this would be true within some narrow temperature limits, which have not yet been found. Enough perchlorate can be obtained by heating a few grams of $KClO_3$ in a tube, until it has melted and the oxygen commences to comes off somewhat rapidly. The tube may then be dropped into water. It will break up. The water should then be boiled up, filtered from the glass particles and allowed to crystallise, after evaporation if necessary, and the crystals boiled with HCl until no more chlorine or ClO_2 is evolved, and finally recrystallised.

In order to distinguish a nitrate in the presence of a chlorate, mix the substance with Na_2CO_3, if other bases than potassium and sodium are present, and ignite until the evolution of oxygen nearly ceases, and test the residue for nitrous acid. The effect of the ignition upon the chlorate is to change it into chloride, and the nitrate into nitrite to some extent. The Cl may be tested for (by adding HNO_3 and $AgNO_3$ to a portion), but this is not evidence of the presence of a chlorate in the original substance, unless chlorides are proved absent. Alkali nitrates and nitrites will withstand a higher temperature than chlorates.

To apply this test for chlorates in the presence of chlorides, an excess of Ag_2SO_4 must be first added to the solution, and the filtrate from the AgCl may then be mixed with Na_2CO_3, evaporated to dryness, and treated as above.

HYPOCHLOROUS ACID, ClHO.—The salts which this acid forms possess considerable interest, on account of the powerful bleaching action which they exert in the presence of acids. Sodium

and calcium hypochlorites are obtained, along with the corresponding chlorides, by passing chlorine through a cold solution of the carbonate or hydroxide. An important compound closely related to the hypochlorites is the so-called calcium chlorohypochlorite (a constituent of chloride of lime or bleaching powder), which appears to be formed according to the equation : $Ca(HO)_2 + Cl_2 = Ca(OCl)Cl + OH_2$.

Hypochlorites are gradually decomposed on exposure to air, with liberation of chlorine, owing to the action of the carbon dioxide contained in air, and it is on this account that hypochlorites are of such great value as disinfectants and bleaching agents.

Dry Reactions.

Hypochlorites, when heated, are converted into chlorates and chlorides, thus : $6Ca(OCl)Cl = 5CaCl_2 + Ca(ClO_3)_2$.

Reactions in Solution.

The calcium, sodium, and magnesium hypochlorites are in common use, as disinfectants or as bleaching agents. The calcium salt is known as "chloride of lime," or bleaching powder.

All hypochlorites are soluble in water. Their aqueous solutions when acidified bleach vegetable colours. On heating or evaporating dilute solutions of hypochlorites, they are partly decomposed into chlorides and chlorates. Dilute acids decompose them, with evolution of chlorine. (Distinction between hypochlorites and chlorates.) Hypochlorites in solution yield oxygen to readily oxidisable subtances, and become converted into chlorides, thus :

$$
\begin{array}{lll}
As_2O_3 & \text{is oxidised to} & As_2O_5. \\
MnCl_2 & ,, \quad ,, & MnO_2, \\
PbO & ,, \quad ,, & PbO_2. \\
PbS & ,, \quad ,, & PbSO_4. \\
\left\{\begin{array}{l}OCOH \\ OCOH\end{array}\right. & ,, \quad ,, & 2CO_2 + OH_2.
\end{array}
$$
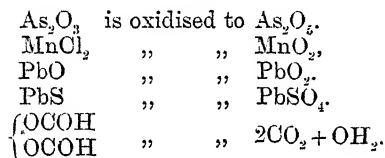
Indigo, litmus, and many organic compounds are readily decolorised or oxidised by hypochlorites, because both chlorine and active oxygen are given off on their decomposition by an acid.

HYDROBROMIC ACID, HBr. — Bromides are decomposed by H_2SO_4 in a similar manner to chlorides, and *some* HBr in a gaseous state is evolved. A secondary action commences, however, very quickly by which some of the HBr becomes oxidised at the expense of the H_2SO_4, and bromine is liberated. *H_2SO_4 does not oxidise HCl.*

(a) $NaBr + H_2SO_4 = NaHSO_4 + HBr$
(β) $2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2$.
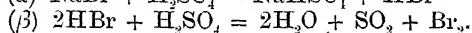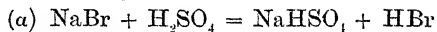
A mixture, therefore, of bromine vapour and HBr gas is usually obtained. A few bromides, as those of AgBr, Hg_2Br_2, are decomposed only slowly by H_2SO_4, but completely by heating with $KHSO_4$. SO_2 passed into bromine water forms HBr and H_2SO_4. As soon as the

water is saturated the HBr comes off steadily as the SO_2 is passed in. The reaction is $Br_2 + 2OH_2 + SO_2 = 2HBr + H_2SO_4$. It is quite quantitative.

Another plan of preparing pure HBr is to decompose PBr_3 (phosphorous bromide) by water, thus :

$$PBr_3 + 3OH_2 = H_3PO_3 + 3HBr.$$
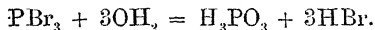
Water is "dropped" into PBr_3, contained in a small retort or distilling flask, from a dropping funnel, and the escaping HBr led into cold water.

The phosphorous bromide is prepared by the action of bromine upon phosphorus in a CS_2 solution. The CS_2 is distilled off on a water bath, and the residual PBr_3 distilled by itself.

PBr_3 can also be made from amorphous phosphorus treated with bromine as above. The HBr can be collected by downward displacement as with HCl.

Similar experiments should be made with it as with HCl gas (*ante*).

Dry Reactions.

Most bromides remain unaltered when ignited ; others are volatilised without decomposition. $AuBr_3$ and $PtBr_4$ are decomposed upon ignition into metal and bromine, which volatilises. Many bromides are changed upon ignition with free access of air, being converted into oxides and free bromine ; others, such as Al_2Br_6,* &c., are decomposed, on evaporation of their aqueous solutions, into oxides and hydrobromic acid. KBr and NaBr are converted, to a great extent, into KCl and NaCl, on repeated ignition with ammonium chloride. When fused with hydrogen potassium sulphate bromides are decomposed into sulphates, with evolution of sulphur dioxide and bromine.

Bromides heated before the inner flame of the blowpipe on a bead of microcosmic salt, in which a little cupric oxide has been diffused, impart a blue colour to the flame, which passes into green, especially at the edges. The difference between chlorides and bromides in this reaction is not very marked.

Reactions in Solution.

A solution of potassium bromide, KBr, may be employed.

Metallic bromides can be divided into :

1st. Bromides which are insoluble in water, such as $AgBr$, Hg_2Br_2, $PbBr_2$ (less soluble in water than $PbCl_2$) ; and—

2nd. Bromides which are soluble in water, comprising most other bromides ; and—

3rd. Bromides, *e.g.*, $SbBr_3$, $BiBr_3$, which are decomposed by water into insoluble oxybromides, SbOBr, BiOBr, and hydrobromic acid. They resemble in this respect the corresponding chlorides.

In order to detect hydrobromic acid or a soluble bromide, add a solution of a silver salt to the solution, when a yellowish white

* The corresponding chlorides and iodides are similarly decomposed.

precipitate of silver bromide, AgBr, is formed, which is insoluble in dilute nitric acid, somewhat soluble in concentrated ammonium hydroxide, readily soluble in potassium cyanide or sodium thiosulphate. .

AgBr is best decomposed by heating in an ignition tube with alkali carbonates (free from chlorides). The aqueous extract is tested for hydrobromic acid, and the insoluble residue for silver.*

In the absence of any well-marked distinguishing features in the silver bromide precipitate, it is preferable to liberate bromine from soluble bromides, and to cause the reddish brown vapour to act upon starch paste, with formation of yellowish bromide of starch.

Nitrous acid (or a nitrite and dilute sulphuric acid) does not liberate any bromine from pure soluble bromides. (Distinction
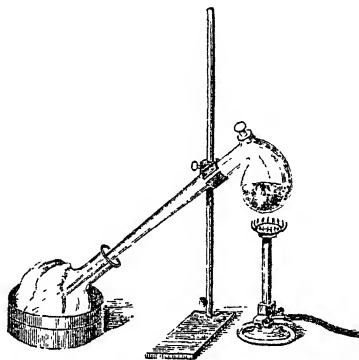
FIG. 93.

between bromides and iodides.) All bromides are, however, decomposed by chlorine, with evolution of bromine, which remains dissolved in the aqueous solution. On shaking with a little chloroform or bisulphide of carbon, the bromine is taken up, and forms a yellowish red liquid, which sinks in the saline aqueous solution.

BROMINE is obtained from natural bromides, such as potassium, magnesium, and calcium bromides, by reactions analogous to those employed for the preparation of chlorine from common salt; for instance, by distilling with manganic oxide and strong sulphuric acid, thus:

$$2KBr + MnO_2 + 2H_2SO_4 = Br_2 + K_2SO_4 + MnSO + 2OH_2;$$
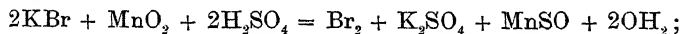
or by distilling a bromide with potassium dichromate and sulphuric acid, thus:

$$6KBr + K_2Cr_2O_7 + 7H_2SO_4 = 3Br_2 + Cr_2(SO_4)_3 + 4KlSO_4 + 7OH_2.$$
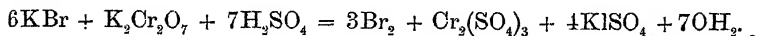
* AgBr is very soluble in solutions of KBr, NaCl, HCl, KI. Water precipitates it again from these.

18

A mixture of a bromide and manganic oxide, or potassium dichromate, is introduced into a tubulated retort (Fig. 93), with concentrated sulphuric acid diluted with its own weight of water, and gently heated over a gas flame. The reddish brown vapour of bromine passes over, and condenses in a flask (which should be kept cold by a stream of water, or, better still, in a vessel surrounded with ice (to a reddish brown, heavy liquid).*

Concentrated sulphuric acid alone evolves hydrobromic acid, together with bromine and sulphur dioxide, as a *part* of the HBr is oxidised by the sulphuric acid (*ante*).

Concentrated nitric acid evolves bromine, together with nitrous fumes, thus : $2KBr + 4HNO_3 = Br_2 + 2KNO_3 + N_2O_4 + 2OH_2.$

In the last two reactions the sulphuric and nitric acids act as oxidising agents, performing, in fact, the functions of the manganic oxide and potassium dichromate in the former reactions.

Bromine (like chlorine) is an indirect oxidising agent—*i.e.*, it is eager to combine with hydrogen, and is capable of decomposing water, sulphuretted hydrogen, &c., under favourable circumstances (*e.g.*, sunlight), with liberation of oxygen, sulphur, &c. This property is made use of in the preparation of hydrobromic acid, which cannot be obtained pure by distilling a bromide with sulphuric acid (for reason above seen). By passing sulphuretted hydrogen through bromine mixed with water, a solution of hydrobromic acid is obtained, and sulphur separates, thus : $Br_2 + SH_2 = 2HBr + S.$ This solution always contains some sulphuric acid, owing to a secondary reaction of the bromine upon water, in the presence of nascent sulphur : $3Br_2 + 4OH_2 + S = 6HBr + H_2SO_4$, from which the hydrobromic acid is separated by distillation. The solution distilling over at ordinary pressures contains about 20 per cent. HBr.

It will be inferred from this that the decomposition of water by bromine would be assisted very much by the presence of deoxidising bodies, such as phosphorus, metallic hypophosphites, sulphites, hyposulphites.

Hydrobromic acid can likewise be prepared by distilling an alkali bromide with phosphoric acids, HPO_3, or H_3PO_4.

To detect a chloride in the presence of a bromide, the solution is acidulated with dilute nitric acid and an *excess* of silver nitrate is added. After shaking the precipitate is washed by decantation, and then agitated with very dilute ammonium hydroxide solution, so as not to dissolve all the precipitate. The ammoniacal extract is filtered off and acidulated with nitric acid, when a white precipitate is obtained.

BROMIC ACID, $HBrO_3$.—Is obtained in combination with potassium by adding bromine to a moderately concentrated solution of potassium hydroxide. Potassium bromate crystallises out from the slightly yellowish coloured liquid, and is purified from potassium

* If test-tubes be worked with, then a little ammonium nitrate (10 grms.) or chloride, with its own weight of water, will form a good enough freezing-mixture and can be contained in a small dish

bromide by washing with water and recrystallisation. The reaction takes place according to the equation :

$$3Br_2 + 6KHO = 5KBr + KBrO_3 + 3OH_2.$$

The free acid is obtained by decomposing barium bromate with dilute sulphuric acid.

It is doubtful whether bromates occur in nature. They are also seldom employed or made.

Dry Reactions.

All bromates are decomposed by heat. Some—*e.g.*, those of the alkalies—fuse and evolve oxygen, leaving a bromide ; others, such as zinc and magnesium bromates, leave an oxide and give off oxygen and bromine ; others, again, leave an oxide and a bromide—*e.g.*, lead and cupric bromates. When mixed with readily oxidisable substances, such as carbon, sulphur, &c., bromates deflagrate like chlorates.

Reactions in Solution.

Employ a solution of potassium bromate, $KBrO_3$.

All bromates are soluble in water, silver and mercurious bromates least so.

Dilute sulphuric, nitric, or phosphoric acids liberate from its salts bromic acid, which, however, exhibits great instability and breaks up into bromine, oxygen, and water very rapidly.

Bromates are readily decomposed by deoxidising substances, such as sulphurous and phosphorous acids, sulphuretted hydrogen, &c., with formation of sulphuric and phosphoric acids, sulphur and water, and liberation of bromine. A mixture of potassium bromide and bromate, when acted upon by dilute acids, is decomposed into bromine and water, thus :

$$5KBr + KBrO_3 + 6HCl = 3Br_2 + 3OH_3 + 6KCl.$$
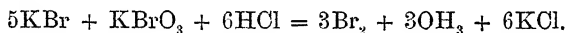
The weak affinity of bromine for oxygen is, moreover, rendered apparent on boiling bromine with such powerful oxidising agents as nitric acid, potassium chlorate or manganate, which are without action upon it.

A bromate in the presence of a chlorate is readily distinguished by precipitation with $AgNO_3$; the white silver bromate, $AgBrO_3$, gives off bromine on being treated with HCl. The residue which bromates and chlorates leave on ignition may also be tested by any of the methods described under hydrochloric and hydrobromic acids.

HYDRIODIC ACID, HI.—Iodides (KI, NaI, MgI_2, CaI_2) occur in sea-water, in the ashes of marine plants, in some mineral springs, and in Chili saltpetre and some borax deposits, from which substances iodine is obtained by processes similar to those employed for the extraction of bromine from bromides.

Very little HI is obtained by acting on an iodide with H_2SO_4, owing to the ease with which HI becomes oxidised by the H_2SO_4. Phosphoric acid and an iodide give more HI.

Dry Reactions.

Most iodides undergo decomposition when heated by themselves, either with or without exclusion of air. Some few give off iodine, and leave the metals; others are partially decomposed, giving off iodine and leaving an oxide of the metal. The alkali iodides, also those of silver and a few others, can be heated to fusion without undergoing any decomposition. Ignition with ammonium chloride converts iodides only partially into chlorides. On fusing cupric oxide in a bead of microcosmic salt, and introducing a little potassium iodide into the bead and heating in the inner blowpipe flame, the outer flame becomes of a fine emerald-green colour.

Reactions in Solution.

A solution of potassium iodide, KI, may be used.

All metallic iodides may be divided into:

1st. Iodides insoluble in water, such as AgI, Hg_2I_2, HgI_2, Cu_2I_2 (BiI_3, AuI_3, PtI_2), and PdI_2; and

2nd. Iodides soluble in water, comprising all others. The iodides of the heavy metals are less soluble than the corresponding bromides or chlorides.

Some elements, the chlorides of which are well known, only form iodine compounds with great difficulty—e.g., sulphur, carbon.

Soluble iodides may be examined in two ways:

1st. By precipitation or conversion of the soluble into insoluble iodides.

$AgNO_3$ gives a yellowish white precipitate of silver iodide, AgI, insoluble in dilute nitric acid, almost insoluble in ammonium hydroxide (partial distinction between HI and HCl), soluble in potassium cyanide or KI, or NaCl or HCl solutions.*

$Hg_2(NO_3)_2$ gives a yellowish-green precipitate of mercurous iodide, Hg_2I_2, very slightly soluble in water, insoluble in dilute nitric acid, soluble in potassium iodide.

$HgCl_2$ gives a beautiful scarlet-red precipitate of mercuric iodide HgI_2, little soluble in water, soluble in alcohol, and soluble also in excess either of mercuric chloride or of potassium iodide. The solutions are colourless.

Lead acetate gives a bright yellow precipitate of lead iodide, PbI_2, dissolving, like the chloride, in hot water (120 parts), to a colourless solution, from which it crystallises out, on cooling, in beautiful shining yellow scales; soluble in dilute nitric acid.

* AgI is very soluble in either the strong haloid acids or in the salts of haloids, especially so in lithium chloride and fluoride. $AgNO_3$ may be dropped into strong KI solution and the AgI formed observed to dissolve immediately. Water or nitric acid reprecipitates AgI. With the latter some $AgIO_3$ is liable to be formed.

Cu_2SO_4 (cuprous sulphate), obtained by treating $CuSO_4$ with SO_2, or adding a sulphite or ferrous sulphate, or boiling the iodide with $CuSO_4$ and metallic copper, produces a dirty white precipitate of cuprous iodide, Cu_2I_2, insoluble in water, sparingly soluble in HCl, soluble in ammonium salts and ammonium hydroxide. *This precipitate is of particular interest, because chlorides and bromides cannot be precipitated in like manner, and because it serves frequently for removing iodine from solutions containing chlorides and bromides.*

2nd. By liberating iodine, and causing the iodine vapour to act upon starch paste. This may be effected in several ways.

On mixing a dilute solution of potassium iodide with a few drops of hydrochloric acid, and then adding a drop or two of a solution of potassium nitrite, iodine is instantly liberated, and may be detected by the yellowish brown tint it imparts to the solution, or, better still, by allowing it to act upon a freshly prepared solution of starch, to which it imparts a fine blue colour. This is one of the most delicate tests. The reaction serves equally well for the detection of HNO_2 (which see), thus :

$$2KI + 2KNO_2 + 4HCl = I_2 + 4KCl + N_2O_2 + 2OH_2.$$
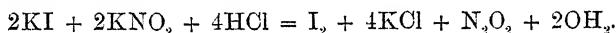
A solution containing free iodine may also be shaken up with a few drops of carbon disulphide, which dissolves the iodine, assuming a fine violet colour. Ether dissolves iodine, but the colour which is produced resembles ether coloured by bromine.

Bromine or chlorine (or what amounts to the same, ClNaO and HCl, or metallic peroxides or perchlorides, *e.g.*, BaO_2, PbO_2, MnO_2 and HCl, or Fe_2Cl_6 and HCl), liberate iodine from iodides. According to the quantity of iodide employed, the iodine separates either as a bluish-black powder, or it merely colours the solution brown.

The methods adopted for the extraction of iodine from metallic iodides are all based upon the expulsion of iodine by oxygen (or its equivalent of chlorine or bromine). Iodine is obtained by distilling an iodide with an oxidising agent and sulphuric acid, *e.g.* :

$$2KI + MnO_2 + 2H_2SO_4 = I_2 + MnSO_4 + K_2SO_4 + 2OH_2, \text{ or}$$
$$6KI + K_2Cr_2O_2 + 7H_2SO_4 = 3I_2 + Cr_2(SO_4)_3 + 4K_2SO_4 + 7OH_2.$$
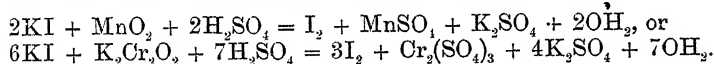
Concentrated acids, such as H_2SO_4, or HNO_3, decompose iodides, with separation of bluish black scales of iodine and evolution of SO_2 or lower oxides of nitrogen, thus :

$$2KI + 2H_2SO_4 = I_2 + K_2SO_4 + SO_2 + 2OH_2.$$
$$2KI + 4HNO_3 = I_2 + 2KNO_3 + N_2O_4 + 2OH_2.$$
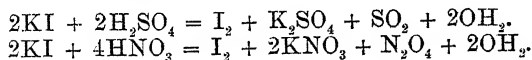
On fusing an iodide with hydrogen potassium sulphate, $HKSO_4$, iodine is likewise liberated, thus :

$$2KI + 4KHSO_4 = 3K_2SO_4 + SO_2 + I_2 + 2OH_2.$$
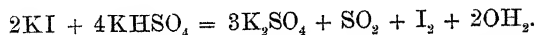
On examining for traces of iodine in aqueous solutions by the action of chlorine, excess should be carefully avoided, as the iodine

may be oxidised by the chlorine to colourless iodic acid, which does not give the blue colour with starch, or the violet colour to the carbon disulphide solution. Previous to this a trichloride of iodine, ICl_3, is very likely formed. The blue colour of iodide of starch is destroyed by various reducing agents, such as SO_2, SH_2, As_2O_3, $SnCl_2$, Hg_2Cl_2, and $HgCl_2$. Alkalies also destroy the colour, but it reappears on acidification. The colour does not show so well in hot solutions.

The destruction of the blue colour of iodide of starch by various reducing agents is due to the decomposition of water by the iodine, with formation of HI, the oxygen being transferred to the reducing agent, thus :

$$H_2SO_3 \text{ (a dilute solution)} + I_2 + OH_2 = H_2SO_4 + 2HI.$$
$$SH_2 \quad + I_2 = 2HI + S.$$
$$H_3AsO_3 \quad + I_2 + OH_2 = 2HI + H_3AsO_4.$$
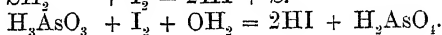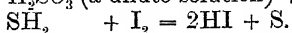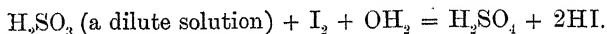
Hydriodic acid solution is usually prepared by acting upon iodine suspended in water (or dissolved in hydriodic acid), with a current of SH_2. Sulphur separates and is removed by filtration, and the solution of hydriodic acid concentrated by distillation. This solution absorbs oxygen from the air, water being formed and iodine liberated, which dissolves in the undecomposed hydriodic acid and imparts a brown colour to the liquid.

Gaseous HI is best obtained by the decomposition of PI_3 by water. PI_3 is made by dropping iodine crystals on to dry phosphorus, either α or β, preferably the latter, as it can be dried in an oven ; PI_3 is formed on very gently warming. This may be made in a flask or test-tube fitted with cork and tube (see *ante*), and a dropping funnel containing water. An excess of phosphorus should be present. HI is a very heavy gas, and fumes more strongly than HBr or HCl in moist air. The tube in which it is collected must be very thoroughly dried. Phosphonium iodide, PH_4HI, is formed as an intermediate product, and is decomposed by water, sometimes with explosive violence. Perform the same series of experiments with HI as with HCl.

The few insoluble iodides may be fused with alkali carbonates, or in the case of AgI and PbI_2 decomposed by means of metallic zinc. The aqueous extract is examined for iodine, and the residue for the metal.

IODIC ACID, HIO_3.—Potassium iodate is obtained, like the corresponding chlorate and bromate, by dissolving iodine in hot potassium hydroxide. The iodate crystallises out first, being much less soluble than KI. The free acid can be prepared by decomposing barium iodate with sulphuric acid, thus :

$$Ba(IO_3)_2 + H_2SO_4 = 2HIO_3 + BaSO_4.$$
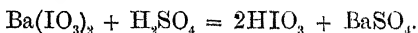
Iodic acid is best obtained by the action of strong boiling nitric acid upon iodine, or by passing chlorine through iodine suspended in water or dissolved in an alkali iodide. This product is not pure.

In addition to HIO_3, there are some higher oxidation products and the anhydride, I_2O_5.

Iodates are said to exist in sea-water.

Dry Reactions.

All iodates are decomposed upon ignition, some breaking up into an iodide, with evolution of oxygen ; others into metallic oxides, iodine and oxygen being expelled. When heated with charcoal they explode less violently than chlorates or bromates.

Reactions in Solution.

A solution of potassium iodate, KIO_3 is used.

$BaCl_2$ gives a white precipitate of barium iodate, nearly insoluble in water and difficultly soluble in dilute nitric acid.

$AgNO_3$ produces a white crystalline precipitate of silver iodate, sparingly soluble in water and in dilute nitric acid, readily soluble in ammonium hydroxide (distinction from HI). On the addition of a reducing agent, e.g., SO_2, to the clear ammoniacal solution of silver iodate a yellowish precipitate of AgI is obtained, thus :

$$AgIO_3 + 3H_2SO_3 = AgI + 3H_2SO_4.$$
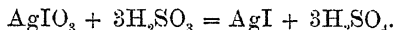
Potassium iodate is decomposed by SH_2, with formation of potassium iodide and sulphuric acid, and precipitation of sulphur ; by H_2SO_3, with separation of iodine, which (by the decomposition of water) is converted into hydriodic acid.

An iodate and iodide act upon each other in the presence of weak acids (e.g., acetic acid), with liberation of iodine. Traces of an iodate in potassium iodide can, therefore, be detected by means of the starch reaction.*

Iodates which give off iodine when they come in contact with various reducing agents, e.g., SO_2, $Na_2S_2O_3$, $SnCl_2$, differ, however, in a marked manner from chlorates and bromates by remaining unacted upon by concentrated sulphuric acid, unless the action be assisted by deoxidising agents, such as ferrous salts, &c.

HYDROFLUORIC ACID, HF.—Fluorine minerals, as CaF_2, $Al_2F_6(NaF)_6$, yield HF by the action of strong acids (sulphuric, phosphoric). No compound of F and O alone is known, although some metallic oxides form with it oxyfluorides.

Dry Reactions.

Heated out of contact with the air, most fluorides melt, but otherwise remain unchanged. Volatile fluorides can be distilled ; but when heated in a moist atmosphere, or if water be added, they are decomposed into oxides (oxyfluorides) and hydrofluoric acid. The changes which fluorides undergo in the dry way are of two kinds.

1st. The fluoride gives off hydrofluoric acid gas, which corrodes

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* Commercial KI almost invariably contains some iodate. Before using it should be melted, either alone or, better, with a little charcoal or sugar.

glass.— By heating a fluoride containing water in a piece of combustion tubing, open at both ends, before the blowpipe, the glass around the fluoride is attacked. The experiment may be carried out also by mixing a little microcosmic salt with the fluoride.

By heating a mixture of a fluoride with hydrogen potassium sulphate HF is disengaged, thus :

$$CaF_2 + 2KHSO_4 = CaSO_4 + KSO_4 + 2HF.$$
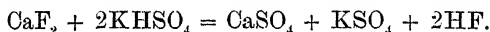
If the operation is done in a test-tube the gas corrodes the upper part of the tube on account of its action upon the silica of the glass, with which it forms a gaseous compound, silicon fluoride, SiF_4, thus : $4HF + SiO_2 = SiF_4 + 2OH_2$. (See "Fluorine.")

2nd. The fluoride is decomposed by hydrogen potassium sulphate in the presence of a borate, with formation of volatile boron fluoride, BF_3.—By heating a mixture * of powdered hydrogen potassium sulphate and fused borax with the finely-powdered fluoride, on the loop
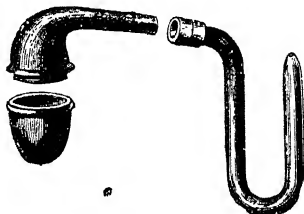
FIG. 94.

of a platinum wire, in the clear flame of a Bunsen gas lamp, boron fluoride is disengaged, imparting a beautiful yellowish green colour to the flame. But this is useless as indicating the presence of HF unless care is taken to distinguish between it and the colour given to the flame by the acid and borax alone.

Reactions in Solution.

Employ a solution of an alkali fluoride.

Most metallic fluorides are solid; others, again, such as the fluorides of the metals whose higher oxides possess acid properties, form volatile, fuming, highly corrosive liquids, or are gaseous at the ordinary temperature. Non-metallic elements form gaseous or liquid fluorides.

Fluorides are either soluble in water and more or less crystalline, such as KF, NaF_2, NH_4F, AgF, SnF_2, Fe_2F_6, HgF_2, Al_2F_6, or insoluble or very sparingly soluble in water, and amorphous when obtained by precipitation—e.g., CaF_2, BaF_2, PbF_2, ZnF_2, CuF_2.

The reactions which a soluble fluoride gives by double decomposi-

* 10 mol. of $KHSO_4$ ($=10 \times 136$).
   3 mol. of CaF_2 ($= 3 \times 78$).
   1 mol. of $B_4O_7Na_2$ 202.

tion with solutions of salts whose metals form insoluble fluorides are not very characteristic.

$BaCl_2$ produces a bulky white precipitate of barium fluoride, BaF_2, soluble in hydrochloric acid, and in much ammonium chloride.

$CaCl_2$ (or $Ca(HO)_2$) gives a gelatinous translucent precipitate of calcium fluoride, CaF_2, which becomes more marked by the addition of ammonium hydroxide. CaF_2 is slightly soluble in cold hydrochloric or nitric acid, more soluble in boiling hydrochloric acid, less soluble in acetic acid, insoluble in free hydrofluoric acid, soluble to some extent in ammonium chloride.

$AgNO_3$ produces no precipitate. (Distinction between HF and HCl.)

It is preferable to test for HF by the reactions based upon the formation of gaseous SiF_4 or BF_3.

All fluorides (soluble or insoluble) are decomposed on heating with concentrated sulphuric acid, with disengagement of HF, a metallic sulphate being left, thus: $CaF_2 + H_2SO_4 = 2HF + CaSO_4$.

The preparation of hydrofluoric acid is best performed by treating the fluoride with sulphuric acid in a small leaden cup heated over a water-bath (Fig. 94), and connected with a leaden **U** tube, surrounded with ice, for the condensation of the acid.

Hydrofluoric acid gas is highly corrosive, and should not be inhaled. If it come in contact with silica (*e.g.*, in glass), SiF_4 is formed, and the glass becomes corroded or etched.

Its reaction upon glass may be shown also by covering a platinum crucible containing a little finely powdered fluoride and concentrated sulphuric acid with a piece of glass, *e.g.*, a watch-glass. The vapour of the evolved hydrofluoric acid corrodes the glass. The action of the hydrofluoric acid becomes apparent when the glass is covered with a thin layer of melted wax, and some design scratched on the waxed side with a pointed instrument. The gas acts upon the unprotected portion of the glass. The design will be found etched more or less deeply into the glass, after the removal of the wax. Mere traces of a fluoride are thus detected, and as no other substance attacks glass similarly the reaction is perfectly characteristic for hydrofluoric acid. It should be remembered, however, that the softer kinds of glass are liable to be corroded by the vapour of ordinary acids alone. In doubtful cases, therefore, it is preferable to employ a glass bulb blown out of combustion glass, or else a plate of rock-crystal.

If the fluoride contains much silica, sulphuric acid disengages silicon fluoride instead of hydrofluoric acid, which does not attack glass; but when passed into water—best by letting the delivery tube dip into a little mercury under the water to keep the tube opening clear—it is decomposed into hydrofluosilicic acid and into $Si(HO)_4$, thus: $3SiF_4 + 4OH_2 = Si(HO)_4 + 2(2HF,SiF_4)$.

This reaction is employed for detecting fluorine in silicates, or if applied to fluorides which are free from silica some finely powdered quartz or glass is first mixed with the fluoride before treating it with sulphuric acid.

The experiment may be performed in a glass flask or small stoneware bottle, provided with a wide delivery tube, which dips under mercury contained in a small porcelain cup at the bottom of a beaker or glass cylinder. Care should be taken that the inside of the delivery tube remains perfectly dry when the receiving vessel is filled with water. A mixture of one part by weight of finely powdered fluor spar, and one by weight of fine sand is introduced into the glass or stoneware vessel. Seven to eight parts by weight of oil of vitriol are added, and the whole shaken gently together and heated upon a sand-bath. Each bubble of the evolved SiF_4, on passing through the water, is decomposed, with separation of gelatinous silica, which after a time fills the water in the form of a dense jelly. The silica is separated by straining through a cloth from the hydrofluosilicic acid, which may be returned to the glass cylinder, and a fresh quantity of SiF_4 passed through, till the acid solution has become sufficiently concentrated.

Silicates containing fluorides which are not decomposed by sulphuric acid are fused with four parts of fusion mixture. The fused mass is extracted with water and filtered. The filtrate contains the fluorine in the form of alkali fluorides together with the alkali silicates. On slightly acidulating with dilute hydrochloric acid to decompose the excess of alkali carbonates, and then digesting with ammonium hydroxide, $Si(HO)_4$ is precipitated, which can be filtered off, leaving the alkali fluoride. On adding $Ca(HO)_2$ or $CaCl_2$, and digesting at a gentle heat, a gelatinous precipitate of CaF_2 is obtained, which is filtered off, dried, and examined. If phosphoric acid be present the precipitate contains $Ca_3P_2O_8$, as well as CaF_2, which does not, however, interfere with the disengagement of hydrofluoric acid gas.

Insoluble fluorides, *e.g.*, CaF_2, are not completely decomposed by fusion with alkaline carbonates unless SiO_2 be present.

HYDROFLUOSILICIC ACID, $2HF,SiF_4$.

—Obtained by passing silicon fluoride into water and separating the precipitated silica by filtration.

It forms salts, called silicofluorides, or fluosilicates, on acting upon metallic oxides, hydrates, or metals, such as Fe or Zn (these latter with evolution of hydrogen), of which the potassium and barium silicofluorides are insoluble.

Dry Reactions.

Silicofluorides are decomposed by heat into fluorides and silicon fluoride.

Reactions in Solution.

A solution of the acid may be employed.

On evaporating a solution of hydrofluosilicic acid it volatilises, and is decomposed into SiF_4 and $2HF$. The acid ought not, therefore, to be heated in a glass vessel.

A few silicofluorides, $2KF,SiF_4$, $2NaF,SiF_4$. BaF_2,SiF_4,* are diffi-
cultly soluble in water, and are quite insoluble in alcohol. Most
other metallic silicofluorides are readily soluble in water.

$BaCl_2$ precipitates translucent crystalline barium silicofluoride,
BaF_2,SiF_4, which falls out very readily. The precipitation is complete
on the addition of an equal volume of alcohol. Strontium is not
precipitated. (Distinction between barium and strontium.)

KCl gives a translucent gelatinous precipitate of potassium silico-
fluoride, $2KF,SiF_4$.

NH_4OH separates $Si(HO)_4$ and forms NH_4F.

On heating a metallic silicofluoride with concentrated sulphuric
acid hydrofluoric acid is evolved.

PHOSPHORIC ACID, H_3PO_4.—This acid is never met with in
the free state in nature, but in combination with bases, such as
CaO, MgO, Al_2O_3 FeO, Fe_2O_3, PbO, as bone-ash, sombrerite,
coprolite, apatite, wagnerite, wavellite, vivianite, pyromorphite. &c.

Dry Reactions.

Most anhydrous metallic phosphates,† when mixed with dry
sodium carbonate and carbon, or black flux, or heated together with
metallic sodium or magnesium in a narrow ignition tube, yield phos-
phides of these metals, recognisable by the odour of PH_3, which is
given off when they are moistened with water.

Normal phosphates of fixed bases are not decomposed upon
ignition. Mono- and di-hydrogen normal phosphates lose water, and
are converted into pyro- and metaphosphates, thus:

$$(1) \quad 2Na_2HPO_4 = Na_4P_2O_7 + OH_2.$$
<div align="center">Sodium
pyrophosphate.</div>

$$(2) \quad NaH_2PO_4 = NaPO_3 + OH_2.$$
<div align="center">Sodium
metaphosphate.</div>
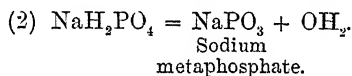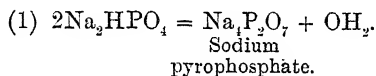
Fusion with caustic or carbonated alkalies converts pyro- and

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* The formulæ of these double fluorides may be written on the same type
as the double chlorides, although, as yet, any absolute proof of "ring" or
cycloid grouping is wanting.
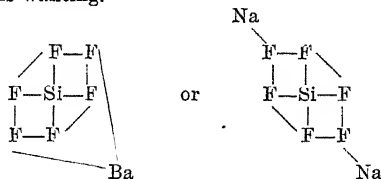
† Many phosphates of the heavier metals as nickel, copper, &c., when
heated to a high temperature with carbon in a closed crucible, yield phos-
phides which, as a rule, are fusible at high temperatures, such as 800° to
1000° C. Zinc phosphide vapourises at about 800° C., but most other metallic
phosphides are fixed at that temperature.

metaphosphates into normal or orthophosphates.   Boiling with acids also effects this conversion.

Alkaline earthy phosphates are only partially decomposed by fusion with alkali carbonates ; most others, *e.g.*, magnesium, ferric, zinc, nickel, manganous, cupric phosphates are completely decomposed.   The residue contains trisodium and tripotassium phosphates. $Al_2P_2O_8$ can only be decomposed by fusion with silica or sodium silicate (water glass) and fusion mixture,* being converted into sodium aluminium silicate and trisodium phosphate.   (Comp. " Aluminium Compounds.")

Reactions in Solution.

Employ a solution of hydrogen disodium phosphate, HNa_2PO_4. Phosphates may be divided into :

1st. Phosphates which are soluble in water, comprising the alkali phosphates only ; their solutions react alkaline ; and

2nd. Phosphates which are insoluble in water, but soluble in mineral acids (some also in acetic acid), comprising all other metallic phosphates.

The following are some of the more important reactions by double decomposition :

$BaCl_2$ yields a white precipitate of hydrogen barium phosphate, $BaHPO_4$, difficultly soluble in ammonium chloride, soluble in nitric or hydrochloric acid.

$CaCl_2$ or $CaSO_4$ produces a white precipitate of calcium phosphate, $Ca_3P_2O_8$, readily soluble in mineral acids ; soluble in acetic acid, when freshly precipitated ; slightly soluble in ammonium chloride.

In dilute solutions of phosphates, Na_2HPO_4, for instance, calcium chloride sometimes fails to produce a precipitate. This may be due to the slight decomposition of calcium chloride in solution in water into calcium oxychloride and HCl, which retains the calcium phosphate in solution ; or to the formation of an acid calcium phosphate, $CaHPO_4$. Addition of ammonium hydroxide brings down the precipitate $Ca_3P_2O_8$ in all cases.

$MgSO_4$ (or, better still, $MgCl_2$), in the presence of ammonium chloride and hydroxide produces a white, crystalline, quickly subsiding precipitate of ammonium magnesium phosphate, NH_4MgPO_4 + $6Aq$, insoluble in ammonium hydroxide, readily soluble in acids, even acetic acid.   A dilute solution of a phosphate is only precipitated after some time.   The precipitation is promoted by stirring and allowing the liquid to stand in a warm place, when the precipitate is seen to adhere, in the form of white streaks, to those parts of the glass vessel which have been touched by the glass rod.   Arsenic acid gives a similar precipitate.

$AgNO_3$ gives a light yellow precipitate of silver phosphate, Ag_3PO_4, soluble in ammonium hydroxide and in nitric acid.

Lead acetate produces a white precipitate of lead phosphate, $Pb_3P_2O_8$, readily soluble in nitric acid, almost insoluble in acetic acid,

* One part of SiO_2, together with six parts of fusion mixture.

as well as ammonium hydroxide. If the precipitate is fused before the blowpipe on charcoal, the bead appears crystalline on cooling ; no reduction to the metallic state takes place.

Fe_2Cl_6 gives a yellowish white gelatinous precipitate of ferric phosphate, $Fe_2P_2O_8$, soluble in hydrochloric acid. The precipitate is somewhat soluble in excess of ferric chloride.

When phosphoric acid has to be removed from a phosphate dissolved in hydrochloric acid—*e.g.*, from the alkaline earthy phosphate $Ca_3P_2O_8$—the free acid is nearly neutralised and then sodium acetate is added, which by double decomposition with the free hydrochloric acid forms sodium chloride and free acetic acid, in which the precipitate, produced by a slight excess of ferric chloride, is insoluble. The mixture is heated nearly to boiling ; a reddish brown precipitate is obtained, which contains the whole of the phosphoric acid, together with some basic ferric acetate. It must be filtered hot, and washed with hot water; the filtrate contains the alkaline earthy bases as chlorides.

Small quantities of phosphoric acid, in the presence of large amounts of a ferric salt, such as are met with in solutions of iron ores, of pig-iron, steel, &c., are best removed by first reducing the ferric to ferrous salt by boiling with *sulphurous acid,* nearly neutralising with sodium carbonate, and lastly adding sodium acetate and a few drops of ferric chloride (or by reoxidising a small portion of the ferrous salt by the addition of a little chlorine water, or a drop or two of bromine water). The phosphoric acid is precipitated on warming. Loss arising from the solvent action of ferric acetate is avoided, as ferrous acetate does not dissolve ferric phosphate.

H_3AsO_4 exhibits with ferric chloride a similar reaction, and has therefore to be separated from an acid solution, by reduction with sulphurous acid and precipitation by a current of SH_2 gas.

Small amounts of phosphorus (usually found in soils as phosphoric acid), in iron ores, pig-iron, steel, copper, &c., may also be precipitated, after dissolving the ore or metal in hydrochloric and nitric acids, whereby the phosphorus is converted into H_3PO_4, and, after driving off the excess of acids by evaporation and taking up the residue with concentrated nitric acid, by adding a solution of ammonium molybdate and concentrated nitric acid (silicic acid is separated by evaporation to dryness; and arsenic acid, if present, should be first removed by sulphuretted hydrogen). On digesting the solution at a gentle heat (60° C.) (for some hours is necessary), a bright yellow precipitate of ammonium phospho-molybdate is obtained. The constitution of this precipitate is somewhat complicated ; it contains molybdic acid, ammonia, and phosphoric acid, MoO_3, 90·7 p.c.; P_2O_5, 3·1 p.c.; $(NH_4)_2O$, 3·6 p.c.; and OH_2, 2·6 p.c. after drying at 100° C. By washing the yellow precipitate with a solution of ammonium molybdate, and lastly with a solution of ammonium nitrate, and then dissolving it in ammonium hydroxide, filtering, and adding NH_4Cl, NH_4OH, and $MgSO_4$, the phosphoric acid is obtained as NH_4MgPO_4 (see *ante*).

White of egg (albumen) is not coagulated by tribasic phosphoric

acid, nor by a solution of an orthophosphate acidulated with acetic acid.

PYROPHOSPHORIC ACID, $H_4P_2O_7$.—Pyrophosphates are obtained by heating monhydric phosphates. They are of little importance, however, since they are not usually met with in natural compounds, and as they are speedily hydrolysed by the action of acids and alkalies into tribasic phosphates.

Reactions in Solution.

Employ a solution of sodium pyrophosphate, $Na_4P_2O_7$.

Alkali pyrophosphates are soluble in water.

All others are insoluble in water, but soluble in dilute acids.

The presence of a soluble pyrophosphate is indicated on adding $AgNO_3$, which gives a white precipitate of silver pyrophosphate, $Ag_4P_2O_7$, soluble in nitric acid or ammonium hydroxide.

Albumen is not coagulated by the free acid, nor by an acetic acid solution of a pyrophosphate.

$(NH_4)_2MoO_4$ (ammonium molybdate) does not give a precipitate until by the action of mineral acids the pyrophosphate has been converted into a normal phosphate.

METAPHOSPHORIC ACID, HPO_3, is distinguished from the tetra- and tribasic acid as follows :

Albumen gives an abundant white precipitate with the free acid and with soluble metaphosphates on the addition of acetic acid.

Magnesia mixture fails to precipitate soluble metaphosphates.

$AgNO_3$ produces a white precipitate of silver metaphosphate.

In the ordinary course of analysis both pyro- and metaphosphates are converted into normal phosphates, and their tetrabasic and monobasic nature is lost sight of. They can, therefore, only be detected by special experiments.

PHOSPHOROUS ACID, H_3PO_3 (dibasic).—Phosphorous anhydride, P_2O_3, is obtained by the slow oxidation of phosphorus on exposure to dry air at the ordinary temperature. By combining with water it forms a very weak acid. With bases it forms phosphites.

Dry Reactions.

Heated by themselves on platinum foil, phosphites are decomposed, burning with a bright flame. Heated in a retort, they evolve hydrogen, mixed towards the end of the decomposition with PH_3, and are converted into phosphates.

Reactions in Solution.

A solution of hydrogen sodium phosphite, HNa_2PO_3, may be employed.

Alkali phosphites are soluble in water.

All other phosphites are, for the most part, difficultly soluble or insoluble in water, but soluble in acetic acid (lead phosphite excepted).

Phosphites (as well as hypophosphites) are of interest, mainly on account of the powerful reducing action which they exert upon salts of various metallic oxides, capable of forming lower oxides, or of being reduced to the metallic state, as well as upon the lower oxides, &c., of metalloids, e.g., SO_2.

$AgNO_3$ is reduced thereby to metallic silver, especially in the presence of ammonium hydroxide and on the application of a gentle heat.

$HgCl_2$ and $Hg_2(NO_3)_2$ are reduced to Hg_2Cl_2 and metallic mercury.

SO_2 forms a phosphite, with liberation of sulphur and evolution of SH_2.

If a phosphite be mixed with zinc and dilute HCl, a mixture of hydrogen and PH_3 is evolved, which fumes in the air and burns with an emerald-green colour. On passing the gases through a solution of silver nitrate a precipitate of silver phosphide and metal is obtained.

The difficultly soluble phosphites of Ba, Ca, Pb, &c., are obtained by double decomposition, the latter salt being insoluble in acetic acid.

HYPOPHOSPHOROUS ACID, $H.H_2PO_2$ (monobasic).—Obtained by the action of alkalies or hydroxides of the alkaline earthy bases upon α-phosphorus and water.

$$P_4 + 3OH_2 + 3KHO = 3(KH_2PO_2) + PH_3.$$
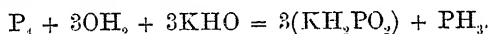
Dry Reactions.

Hypophosphites are decomposed upon ignition into pyrophosphates and PH_3: $4KH_2PO_2 = K_4P_2O_7 + 2PH_3 + OH_2$.

Reactions in Solution.

A solution of potassium hypophosphite may be employed.

All hypophosphites are soluble in water. They constitute even more powerful reducing agents than the phosphites.

Nitric acid or chlorine water changes them into phosphates.

H_2SO_4 is reduced to H_2SO_3, partly even to sulphur.

$CuSO_4$ is reduced to metallic copper or cupric hydride, CuH_2.

$HgCl_2$ is reduced to Hg_2Cl_2, and then to mercury.

$AuCl_3$ and $AgNO_3$ yield the metals.

$Zn + H_2SO_4$ (nascent hydrogen) yield H_2 and PH_3.

In the ordinary course of analysis both phosphorous and hypophosphorous acids are converted into phosphoric acid, and they must therefore be identified by the special reactions just described.

Their soluble salts will act as photographic developers, but are inconvenient substances to obtain and work with.

SILICIC ACID (H_4SiO_4) (?).—Silicic anhydride or silica, SiO_2, occurs in nature both in a crystalline and amorphous condition, either in the free or combined state. Quartz and rock-crystal are composed of almost pure crystalline silica. Opal, hyalite, and some other

minerals consist of amorphous silica, and are probably derived from silicon hydrates by a process of slow dehydration. Other silicious bodies, such as chalcedony, agate, flint, are principally composed of amorphous silica, or of a mixture of the two.

The compounds of silica with bases, especially with OK_2, ONa_2, CaO, MgO, Al_2O_3, FeO, MnO, are exceedingly numerous, and vary to a very great extent in their constitution and properties.

Dry Reactions.

Both varieties of silica are characterised by their infusibility when heated by themselves before the blowpipe, or in a bead of microcosmic salt. Pure silica fuses with sodium carbonate to a clear glass, which, if sufficient silica has been used, remains transparent on cooling. Silicates rich in silica behave like pure silica. If a fragment of a silicate is heated with microcosmic salt, its base or bases are dissolved, while the silica is seen to float about in the liquid phosphate bead as a silica skeleton. Silicates containing coloured oxides give rise to opalescent beads in which the SiO_2 can be distinguished only with difficulty.

When silica, or a silicate rich in silica, is heated on platinum wire before the blowpipe with sodium carbonate, the SiO_2 displaces the CO_2, and forms a clear glass of sodium silicate. The alkali carbonate should not be employed in excess. Calcium and magnesium silicates do not dissolve to a clear bead as a rule.

Beyond identifying silica and obtaining a general knowledge of the nature of any silicate under examination, respecting its fusibility, state of hydration, &c., the blowpipe reactions fail to supply distinguishing tests regarding the chemical composition of these bodies, since a very large number of silicates differ from each other merely in the relative proportions of their component metallic elements.

Reactions in Solution.

Silicates may be divided into :

1. Silicates which are soluble in water, including only potassium and sodium silicates ; and

2. Silicates insoluble in water, including all others.

These latter silicates are either soluble in concentrated hydrochloric or sulphuric acid, or partly soluble and partly insoluble, or, lastly, insoluble in these acids.

All insoluble silicates are attacked by hydrofluoric acid, with disengagement of silicon fluoride, or by fusion mixture (or caustic baryta) at a high temperature.

By treating an aqueous solution of sodium silicate, Na_2SiO_3, with dilute hydrochloric acid, it is decomposed into NaCl and H_4SiO_4. The latter remains either dissolved in the acid, or is partially separated in a colloid or gelatinous form. On heating in a porcelain dish over a water-bath, the gelatinous mass becomes firmer, and can be broken up, by means of a glass rod, into lumps, which speedily lose their water, leaving anhydrous silica. The dried

mass is treated with a little concentrated hydrochloric acid and hot water, when NaCl is dissolved out (together with small quantities of Al and Fe—impurities in the sodium silicate), and the silica remains insoluble. ·

Ammonium chloride or carbonate precipitates H_4SiO_4 from a solution of sodium silicate. Salts of most of the heavy metals, as well as of the alkaline earthy metals, form by double decomposition with a soluble silicate white or yellowish white silicates,* soluble in dilute hydrochloric or nitric acid, which, however, possess no characteristic properties. It is therefore necessary to remove the silica in order to detect bases, by evaporating to dryness with hydrochloric acid. On digesting the dry mass with a little hydrochloric acid, the metallic oxides are dissolved, and can be separated by filtration from the silica. SiO_2, like P_2O_5, is detected whilst testing for bases.

Most natural and artificial silicates are insoluble in water. Many, e.g., zeolites, as well as certain artificial silicates, such as slags from blast furnaces, &c., are decomposed on digesting the finely powdered silicate with concentrated hydrochloric acid.

Silicates, such as kaolin and clays, which are not attacked by hydrochloric acid can frequently be decomposed, either partially or wholly, by hot concentrated sulphuric acid diluted with about one-third of its weight of water ; many natural silicates yield more or less silica on treat-

FIG. 95.

ment with hydrochloric acid, which silica may be taken to represent the soluble silica or the decomposable silicates, leaving the greater portion of the mineral behind in its original condition.
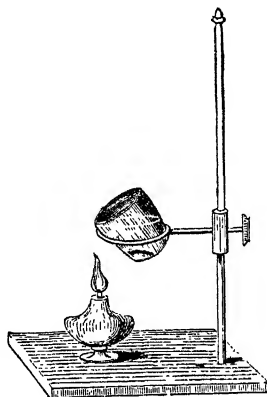
Silica, or silicates insoluble in acids, forming by far the greater number, are readily attacked by gaseous hydrofluoric acid, or by fluor spar and H_2SO_4, gaseous SiF_4 being given off. This method may be resorted to when alkalies are present in a silicate, as, e.g., in felspar. A little of the finely powdered silicate is moistened with strong ammonia, put into a platinum crucible or small platinum capsule, and exposed to the action of gaseous H.F. This gas should be generated in a leaden or platinum vessel. The platinum crucible is to this end supported on a lead tripod in a small leaden basin, which can be closed with a lid of the same metal. A layer of fluor spar is put at the bottom of this vessel, mixed and covered with concentrated sulphuric acid. The leaden vessel, after being covered, is placed for a day or two in a warm place. The crucible is then taken out, and its contents cautiously evaporated by applying a

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* Calcium or barium silicates formed in this manner are useful as preservatives of the surfaces of buildings of dolomitic limestone, &c., against the action of gases, as SO_2, contained in the smoky air of towns.

19

gentle heat, as shown in Fig. 95, from the upper part of the crucible downward, till the whole of the ammonium fluoride has been driven off. The dry residue is dissolved in hydrochloric acid and tested for bases. A small residue is usually left, which is filtered off and treated once more in the same manner.

An expeditious way of detecting SiO_2 with certainty is to warm a little of the finely powdered mineral, mixed with fluor spar, with strong sulphuric acid in a piece of lead tube closed at one end, and bent almost into a U form, with the open limb shorter than the other. On arranging this to dip only just below the surface of water in a small beaker, and applying heat to the closed limb containing the mixture, SiF_4 will be given off, and form gelatinous SiO_2 on contact with the water.

The same result may be obtained more expeditiously by treating the mineral in a platinum crucible with liquid hydrofluoric acid, and evaporating cautiously in a well-ventilated draught closet. The residue is dissolved in hydrochloric acid. Any insoluble part which may be left is separated by filtration and treated again with hydrofluoric acid. This treatment has generally to be repeated several times before the whole of the bases are obtained in a soluble condition.

Treatment with CaF_2 and concentrated H_2SO_4 is sometimes objectionable, on account of the formation of insoluble $CaSO_4.OH_2$.

A less cumbersome yet equally satisfactory method for decomposing silicates in order to detect the alkalies in them is the following: Mix ·5 grm. of finely powdered silicate intimately with ·5 grm. of pure NH_4Cl, and then with 4 grms. of pure precipitated granular calcium carbonate,* and heat the mixture in a platinum crucible, first gently, and by means of a small Bunsen flame, till the ammonia is volatilised. Then apply a stronger heat, and, lastly, heat for half an hour over a good bunsen flame. The sintered mass consists now of caustic lime, disintegrated silicate (rendered soluble in acids), and alkali chlorides soluble in water, besides $CaCl_2$. It is next slaked and repeatedly extracted with small quantities of hot water at a time. The liquid after filtration is free from silica and contains the alkali metals as chlorides. The lime in solution is removed by precipitation with ammonium oxalate and hydroxide, and the filtrate evaporated to dryness and gently ignited, when the fixed alkali salts are left behind.

All silicates insoluble in water and acids may be decomposed by fusion with alkali carbonates (fusion mixture). They are first ground up very finely in an agate mortar, then intimately mixed with three or four times their weight of fusion mixture, and heated in a platinum crucible as long as any CO_2 is given off. This may be done over a good bunsen flame, or by means of a gas blowpipe. (A platinum crucible can be employed with safety only when the absence of easily reducible and fusible metals has been established

* Prepared by precipitating a dilute solution of $CaCl_2$ at 70° C. with excess of ammonium carbonate, and washing the precipitate thoroughly with hot water by decantation.

by a preliminary examination of the silicious substance on charcoal.) The mass is at once treated with dilute hydrochloric acid and evaporated to dryness. The residue is treated with a little HCl, water is added, and the solution of the base filtered from the silica. The alkalies must be examined for in a separate portion by treatment with hydrofluoric acid.

Pure amorphous silica dissolves completely when boiled with an aqueous solution of fixed caustic or carbonated alkalies.

SiO_2 is separated from TiO_2 (titanic anhydride) by fusion with $HKSO_4$, and subsequent treatment with water; the SiO_2 remains undissolved. The TiO_2 is precipitated from the acidulated aqueous solution by long-continued boiling.

BORIC ACID, H_3BO_3 (orthoboric acid).—Is found in nature both combined and in the free state.

Dry Reactions.

Most borates swell up when heated by themselves, and fuse into a transparent glass. The free acid forms scaly crystals, possessing a pearly lustre and feeling peculiarly greasy to the touch.

When heated to 100° C. the crystals lose water and become converted into metaboric acid, HBO_2, and by further heating this acid fuses to a colourless, transparent, glassy-looking mass of boric anhydride, B_2O_3, which can be kept in a fused condition without loss from volatilisation.

A mixture of $KHSO_4$ and a borate, heated on a platinum wire in the blowpipe flame, imparts a green colour to the flame, owing to the liberation of boric acid.

To detect small quantities of boric acid before the blowpipe, the borate is powdered and mixed with $KHSO_4$ and CaF_2.* The mixture is made into a stiff paste with a few drops of water, and cautiously introduced, on the loop of a platinum wire, into the inner blowpipe flame, when the outer flame acquires momentarily a yellowish green tint, owing to the volatilisation of boric fluoride, BF_3. Phosphates as well as copper salts, when moistened with sulphuric acid and heated in the outer flame, give likewise a green tint to the flame.

Reactions in Solution.

A solution of borax, $Na_2B_4O_7$, is used.

The alkali borates are soluble in water; all others are difficultly soluble, but none are absolutely insoluble. All borates dissolve in acids and ammonium chloride.

The precipitates produced by double decomposition of a soluble alkali borate with salts of the alkaline earths, or with lead, silver, mercurous, or ferrous salts, &c., are white or yellowish white, and are readily soluble in acids and ammonium chloride.

The free acid dissolves in water and alcohol, and its solutions

* Three to four parts of the flux (consisting of one part of powdered CaF_2 and four and a half to five parts of $KHSO_4$).

impart to a bunsen gas flame a fine green colour. An alcoholic solution inflamed in a porcelain dish, or, better still, in a test-tube, gives the same characteristic flame, and the colour becomes all the more perceptible when the burning alcohol is stirred with a glass rod. The B_2O_3 is volatile along with the alcohol, which is not the case with other substances, as Cu or Ba salts. A borate mixed with strong sulphuric acid shows the same reaction, but it is preferable to make a paste of the substance with strong H_2SO_4, and to bring a small quantity of this on a platinum wire near to the lower part of a non-luminous flame. The boric acid is shown by the green flame.

A green flame (of a somewhat greenish blue tint, however) is obtained also by heating many metallic chlorides with alcohol and concentrated sulphuric acid (owing to the formation of ethylic chloride, C_2H_5Cl), also by passing hydrochloric acid gas into the flame of burning alcohol.

If a borate cannot be decomposed by sulphuric acid, it is fused with potassium hydroxide, and the fused mass may be extracted with alcohol, or it may be tested as above.

An aqueous solution of boric acid cannot be evaporated without loss of acid from volatilisation.

An alcoholic solution of boric acid colours turmeric paper reddish brown, especially on drying the strips of paper in a warm place (a water-oven). This colour becomes more intense in the presence of hydrochloric or sulphuric acid (even in the presence of nitric or tartaric acid). The colour produced by heating turmeric paper with hydrochloric acid is blackish brown, and must not be confounded with the colour produced by boric acid. The dried paper acquires a green or a blackish tint when touched with alkalies, as NaHO.

Hydrofluoric acid (or H_2SO_4 and CaF_2) decomposes all borates, with formation of volatile boric fluoride, thus :

$$Na_2B_4O_7 + 6CaF_2 + 7H_2SO_4 = 6CaSO_4 + Na_2SO_4 + 4BF_3 + 7OH_2,$$
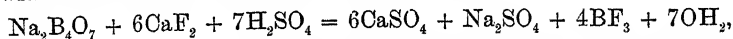
and if the gaseous boric fluoride be passed into water, it forms hydrofluoboric acid, thus :

$$4BF_3 + 3OH_2 = 3(BF_3,HF) + H_3BO_3.$$
$$\text{Hydrofluoboric}$$
$$\text{acid.}$$
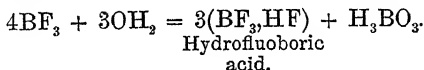
This acid combines with bases, forming borofluorides or fluoborates, thus : $BF_3,HF + KHO = BF_3,KF + OH_2$.

ORGANIC ACIDS.

HYDROCYANIC ACID (prussic acid), HCy.—This acid * consists of hydrogen and the compound radical cyanogen, Cy, molecule

* The compounds which the radicals cyanogen, ferro- and ferri-cyanogen, &c., are capable of forming will be treated somewhat more fully, since a thorough understanding of the various reactions is necessary in order to analyse cyanogen compounds successfully.

$\mathrm{CN}_{\mathrm{CN}}$. It forms salts called cyanides, which are analogous in their chemical constitution to chlorides, bromides, &c. Cyanogen cannot be obtained technically by the direct combination of carbon and nitrogen, although it is formed in the electric arc, but an alkali cyanide results from the action of caustic or carbonated alkalies upon nitrogenous organic bodies, such as fibrin, albumen, and gelatin at a high temperature. Commercial cyanide of potassium contains some cyanate, and generally a large quantity of carbonate.

When organic substances containing nitrogen are heated with sodium or potassium, and some other metals, as Mg or Fe, the two elements C and N seem to be simultaneously liberated, and then combine with the alkali (or other metal) to form a compound which is very stable at a high temperature. In order that the whole of the nitrogen may be resolved into this form, it is necessary for any oxygen present to be fully taken up, either as water by excess of hydrogen, or as CO, carbon monoxide, by carbon. Alkali cyanides are formed in the iron blast furnace.

Dry Reactions.

KCy and NaCy are not decomposed upon ignition in closed vessels, as may be inferred from their mode of manufacture; but when heated with free access of air they are converted into cyanates. The same change takes place, only more speedily, when potassium cyanide is heated with less energetic oxidising agents, such as MnO_2, PbO_2, PbO, CuO, SnO_2, &c., when the metal or a lower oxide is left. Heated in the presence of metallic sulphides, it is converted into potassium sulphocyanate, KSCy. Potassium cyanide is on this account a most valuable deoxidising and desulphurising agent, and is employed in blowpipe reactions whenever a metallic oxide (or sulphide) has to be reduced to the metallic state. Cyanides of the heavy metals undergo decomposition upon ignition; some (e.g., the cyanides of the noble metals) break up into metal and cyanogen gas; others into the metal, carbon, and nitrogen (e.g., the cyanides of iron); others, again (such as AgCy, $HgCy_2$, $CuCy_2$, $ZnCy_2$), yield cyanogen gas, metallic silver, mercury, &c., and paracyanogen—a brownish black substance, which is polymeric with cyanogen, usually expressed by the symbol Cy_n.

This behaviour of solid cyanides furnishes ready means of preparing cyanogen gas, either by igniting dry $HgCy_2$, or AgCy; or by heating two parts of dry yellow prussiate of potash, or potassium ferrocyanide, K_4FeCy_6, with three parts by weight of dry $HgCl_2$.

CYANOGEN, * $\begin{cases} \mathrm{CN} \\ \mathrm{CN} \end{cases}$. Melting-point, $-34 \cdot 4^\circ$ C.; boiling-point, $20 \cdot 7^\circ$ C. Relative weight, gas $= 1 \cdot 799$; liquid $= \cdot 866$.—It is a colour-

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* Cyanogen gas should on no account be prepared unless for some special purpose, and with every precaution against breathing the gas, owing to its fearfully poisonous nature. Cyanogen and its compounds with the alkali metals are extremely stable bodies at a high temperature. Great chemical

less gas of peculiar odour, burning with a beautiful purple or peach-blossom coloured flame, and yielding CO_2 and N. The gas is nearly twice as heavy as air, and since water dissolves about four times its own volume it must be collected over mercury, or by downward displacement. In $CHCl_3$ or CCl_4 it is much more soluble. An aqueous solution decomposes spontaneously into a variety of products.* It is one of the few gases which condense to a liquid at a moderate pressure (3·6 atmospheres).

Cyanogen compounds, when ignited in a tube with excess of soda-lime, give up the whole of their nitrogen as ammonia.

Reactions.

To test a gas for cyanogen it should be shaken up with KHO, which absorbs the cyanogen, forming cyanide and cyanate of potassium, the solution of which may be tested as usual.

It is also absorbed by yellow ammonium sulphide, forming sulpho-cyanate of ammonium, which is easily identified by the dark red colour it gives with ferric salts.

Reactions in Solution.

The cyanides of the alkali metals and alkaline earthy metals are soluble in water, the former readily, the latter with difficulty. The cyanides of the heavy metals are insoluble in water, with the exception of $HgCy_2$; but are for the most part soluble in a solution of potassium cyanide, forming soluble double cyanides, which are frequently crystalline, and which upon ignition are decomposed like single cyanides—i.e., the cyanide of the heavy metals breaks up into metal and cyanogen, or metal, carbon (carbide ?), and nitrogen, whilst the alkali cyanide is not decomposed, and can be dissolved out from the residue.

The following is a list of some of the more important single cyanides—i.e., cyanides which contain only one metal:

Potassium cyanide, soluble in water   .   . KCy.
Sodium   ,,   ,,   ,,   .   . NaCy.

stability is thought to be associated with or to depend upon a more or less symmetrical structure. That of cyanogen may perhaps be represented as
$C\equiv N$ $N=C$ $C\equiv N$
$|$ although an isomeric form is possible $|$ $||$ and even $|$ $||$ which
$C\equiv N$ $N=C$ $C\equiv N$
would be a ring or closed chain formula.

A cyanide might then be
$C\equiv N-K$ $N=C-K$
$|$ or $|$ $|$ which is less in keeping
$C\equiv N-K$ $N=C-K$
with experiment. The cyanogen molecule contains, undoubtedly, "labile" elements.

* It *should* form ammonium oxalate exclusively from the following reactions:

(I) $(NH_4)_2C_2O_4 - 4H_2O = C_2N_2$;
(II) $C_2N_2 + 4H_2O = (NH_4)_2C_2O_4$.
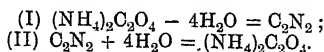
The former can be carried out with the aid of P_2O_5, but the second is somewhat difficult to manage quantitatively.

Barium	,,	difficultly soluble in water	$BaCy_2$.
Silver	,,	insoluble in water . .	$AgCy$.
Zinc	,,	,, ,, . .	$ZnCy_2$.
Cadmium	,,	,, ,, . .	$CdCy_2$.
Nickel	,,	,, ,, . .	$NiCy_2$.
Cobaltous	,,	,, ,, . .	$CoCy_2$.
Cuprous	,,	,, ,, . .	Cu_2Cy_2.
Mercuric	,,	soluble in water . .	$HgCy_2$.

Some of these single cyanides are readily decomposed by acids, with evolution of hydrocyanic acid ; others are more stable.

Double cyanides contain, generally, a cyanide of an alkali metal, K or Na, and another cyanide, as $Zn(CN)_2$ or $Cd(CN)_2$, &c. They seem to resemble to some extent some double chlorides. Most, if not all, the insoluble cyanides are soluble in an excess of an alkali cyanide. (See $AgCy$.)

The action of dilute acids shows clearly the existence of two distinct classes of double cyanides—viz. :

1st. Double cyanides which are readily decomposable, giving off hydrocyanic acid when treated with dilute mineral acids. They possess an alkaline reaction. Their alkali cyanide is decomposed by dilute mineral acids into HCN and a salt of the alkali metal, and into a cyanide of the heavy metal, which remains in combination with the liberated HCN, and this cyanide, being insoluble, is precipitated, or both cyanides are decomposed, and the whole of the HCy is liberated, e.g. :

$$(1)\ KAgCy_2 + HNO_3 = AgCy + HCy + KNO_3.$$
Precipitated.

$$(2)\ K_2ZnCy_4 + 4HCl = ZnCl_2 + 2KCl + 4HCy.$$
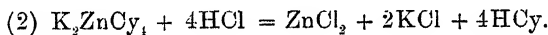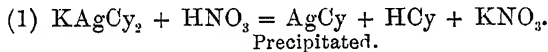
2nd. Double cyanides which possess a neutral reaction and give off no hydrocyanic acid when treated with dilute hydrochloric acid, the negative element of the acid forming a salt with the alkali metal, whilst the hydrogen or positive element, by uniting with the remaining elements, forms a new acid of a more complex nature, thus :

$$K_4FeCy_6 + 4HCl = H_4FeCy_6 + 4KCl.*$$
Hydroferrocyanic
acid.

$$K_6Fe_2Cy_{12} + 6HCl = H_6Fe_2Cy_{12} + 6KCl.$$
Hydroferricyanic
acid.

$$K_6Co_2Cy_{12} + 6HCl = H_6Co_2Cy_{12} + 6KCl.$$
Hydrocobalticyanic
acid.
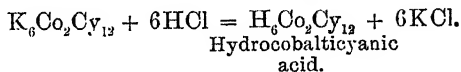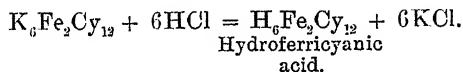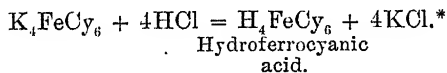
* In these salts (ferro- and ferri- and cobalti-cyanides) the constitution is very likely somewhat akin to that of benzene compounds, and is expressible as a closed chain, ring, or nucleus. Their much great stability, &c., certainly

The single, as well as easily decomposable double cyanides, which yield hydrocyanic acid, when treated with dilute mineral acids, are, moreover, remarkable for their highly poisonous character, whilst these latter—the double cyanides containing a very stable cyanogen radical, *e.g.*, ferrocyanogen, $FeCy_6$, cobalticyanogen, Co_2Cy_{12}—are not poisonous, or not markedly so.

All these complex cyanogen compounds—both decomposable and non-decomposable—may be viewed as double cyanides.

The following list contains some of the more interesting double ·

points to a different structure from that of single and decomposable double cyanides.

Potassium ferrocyanide might, for instance, be pictured as a cyanogen ring,
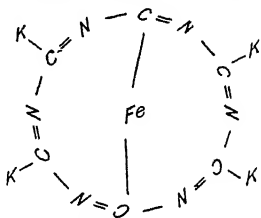
and when this is converted by oxidation into ferricyanide, $K_3Fe(CN)_6$,
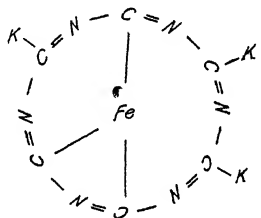
Of course the Fe or Co may be doing quite different work in these compounds from what they are doing in ordinary salts. There is no proof that it may not be tetravalent or hexavalent. Whether the iron is directly united to carbon or nitrogen or to the cyanogen molecule as a whole is all waiting for investigation to settle. In the meanwhile these views do no harm. In ferro and nickel carbonyls the metals can scarcely be otherwise than attached to carbon.

The easily decomposable double cyanides, as K_2ZnCy_4, might be expressed thus :
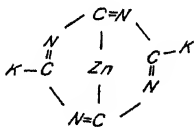
or a less probable form :
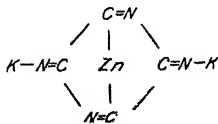
cyanides—*i.e.*, cyanides containing more than one metal—the easily decomposable class being indicated by a comma placed between the cyanogen and the metal:

Potassium zinc cyanide	.	.	.	. K_2Zn,Cy_4.
,,	cadmium cyanide	.	.	. K_2Cd,Cy_4.
,,	nickel ,,	.	.	. K_2Ni,Cy_4.
,,	silver ,,	.	.	. KAg,Cy_2.
,,	aurous ,,	.	.	. KAu',Cy_2.
,,	auric tetracyanide	.	.	. KAu''',Cy_4.
,,	cuprous cyanide	.	.	. $K'_2Cu'_2,Cy_4$.
,,	platinous ,,	.	.	. K_2Pt'',Cy_4.
,,	platinic ,,	.	.	. $K'_4Pt'''_2,Cy_{12}$.
,,	ferrous cyanide (potassium ferro-cyanide, yellow prussiate)			. K_4FeCy_6.
,,	ferricyanide, red prussiate	.	.	. $K_6Fe_2Cy_{12}$.*
,,	cobalticyanide	.	.	. $K_6Co_2Cy_{12}$.*
,,	chromicyanide	.	.	. $K_6Cr_2Cy_{12}$.*
,,	manganicyanide	.	.	. $K_6Mn_2Cy_{12}$.*

If the different behaviour of these double cyanides with dilute acids and with ferroso-ferric salts be noticed, the easily decomposable double cyanides giving a precipitate of Prussian blue, whilst the others—the difficultly decomposable double cyanides—yield no hydrocyanic acid when treated with dilute acids, and produce (with the exception of the ferro- and ferri-cyanogen compounds) no precipitate of Prussian blue with ferroso-ferric salts and hydrochloric acid, it becomes evident that the complex groups of elements, ferrocyanogen, $FeCy_6$, ferricyanogen, Fe_2Cy_{12}, cobalticyanogen, Co_2Cy_{12}, &c., which behave, like cyanogen, as a group or complex, may likewise be viewed as compound radicals, if by this term is denoted a group of common and constant constituents found in a whole series of compounds, and capable of replacing multiples of Cl, Br, &c., in constant atomic proportions.

It is possible to produce by double decomposition precipitates with soluble salts of almost all the heavy metals in which the potassium—or positive radical—is either entirely or partially exchanged for an equivalent quantity of a heavy metal, whilst the negative group of elements remains unaltered, thus:

$$K_4FeCy_6 + CuSO_4 = K_2CuFeCy_6 + K_2SO_4, \text{ or}$$
$$K_4FeCy_6 + 2CuSO_4 = Cu_2FeCy_6 + 2K_2SO_4.$$
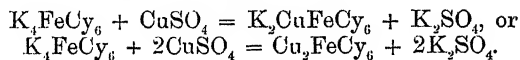
On the addition of an alkali hydroxide or carbonate, the whole of the heavy metal is removed as hydroxide or carbonate, with formation of an alkali ferrocyanide.

Easily decomposable soluble double cyanides give likewise precipitates with solutions of heavy metals, *e.g.*:

$$2KAgCy_2 + ZnSO_4 = Zn_2Ag_2Cy_4 + SO_4K_2;$$
Precipitated.
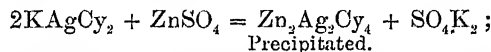
* These formulæ may be halved for simplicity, thus: K_3FeCy_6, &c.

but there is no evidence to show whether these precipitates are real compounds or only mixtures of two insoluble cyanides ; nor is there any proof that alkali hydroxides reproduce the original double cyanide. Dilute sulphuric acid decomposes $ZnCy_2$ in the above precipitate, $AgCy$ being left behind, just as if no connection had existed between the two cyanides, or simply because the $AgCN$ is so insoluble. Alkali hydroxides or carbonates are without action upon easily decomposable cyanides. A few are decomposed by sulphuretted hydrogen, e.g., K_2CdCy_4, K_2HgCy_4, $KAgCy_2$, with precipitation of a metallic sulphide ; in others, such as K_2MnCy_4, K_2NiCy_4, K_2ZnCy_4, and K_2CuCy_4, the metal is only partially precipitated.

It is evident from these changes that easily decomposable and difficultly decomposable double cyanides differ in stability, and this probably depends upon chemical structure as much as upon the individual nature of the metal they contain.

A solution of potassium cyanide, KCy, may be used for the wet reactions.

$AgNO_3$ gives a permanent white curdy precipitate * of silver cyanide, $AgCy$ only, when more than one molecule of $AgNO_3$ has been added for every two molecules of KCy. The precipitate is insoluble in dilute nitric acid, soluble in ammonium hydroxide, sodium thiosulphate, and potassium cyanide. $AgCy$ resembles $AgCl$ so very closely that special experiments are required to distinguish it from the latter, or to detect hydrocyanic acid in the presence of a chloride.

This may be done (1) by boiling with strong HNO_3, which dissolves $AgCy$ but not $AgCl$; (2) by igniting a mixture of $AgCl$ and $AgCy$, which has been entirely freed from silver nitrate by washing with hot water, when $AgCy$ is decomposed into cyanogen, metallic silver, and paracyanogen. $AgCl$ fuses without decomposition. On dissolving the residue in nitric acid and filtering, a precipitate of $AgCl$ is obtained, on the addition of hydrochloric acid, or a soluble chloride, the silver of which must have been present originally as cyanide. (Distinction between HCl and HCy.)

Dilute mineral acids decompose potassium cyanide readily, with evolution of HCy. On decomposing a small quantity of KCy by dilute sulphuric acid in a small porcelain dish, and inverting another small dish containing a drop or two of yellow ammonium sulphide over it, the gaseous hydrocyanic acid, acting upon the ammonium sulphide, forms ammonium sulphocyanate, NH_4SCy, and NH_4HS, thus : $(NH_4)_2S_2 + HCy = NH_4SCy + NH_4HS$. The solution then gives a characteristic blood-red coloration with Fe_2Cl_6.

This constitutes one of the most delicate reactions for free hydrocyanic acid, as well as for soluble or easily decomposable cyanides.

$CuSO_4$ to which a solution of SO_2 has been added, gives with KCy a white precipitate of cuprous cyanide, Cu_2Cy_2, soluble in potassium cyanide ($K_2Cu_2Cy_4$).

* $HgCy_2$ is not precipitated by silver nitrate.

Mercurous nitrate, $Hg(_2NO_3)_2$ gives a grey precipitate of metallic mercury, whilst $HgCy_2$ remains in solution.

Iron salts are among the most delicate reagents for hydrocyanic acid, or for soluble cyanides, on account of their tendency, especially in the presence of potassium hydroxide, to form difficultly decomposable double cyanides (containing the compound acid radicals ferro- and ferri-cyanogen), which are of a characteristic blue colour (hence the name cyanogen, from κύανος, blue, γεννάω, I generate). The solution containing hydrocyanic acid, or a soluble cyanide, is first treated with a little potassium hydroxide, then with a mixture of ferric chloride and ferrous sulphate, and heated. On the addition of dilute hydrochloric acid, in order to dissolve the precipitated ferrous and ferric hydrates, a fine blue precipitate, or in the case of a mere trace of HCy a green coloration only, of Prussian blue is obtained. The changes may be expressed by the equations :

(1) $KHO + HCy = KCy + OH_2$.
(2) $FeSO_4 + 2KCy = FeCy_2{}^* + K_2SO_4$.
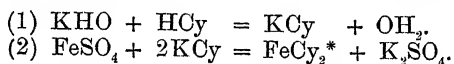
$FeCy_2$, by combining with $4KCy$, forms the soluble double cyanide K_4FeCy_6.

(3) $2Fe_2Cl_6 + 3K_4FeCy_6 = Fe_4(FeCy_6)_3 + 12KCl$.
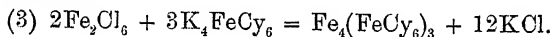
Free hydrocyanic acid dissolves mercuric oxide, with formation of mercuric cyanide, which is not precipitated by alkalies. $HgCy_2$ exhibits considerable stability compared with other cyanogen compounds. (Palladium cyanide is even more markedly stable. A palladium salt will remove cyanogen from $Hg(CN)_2$.) Boiling dilute H_2SO_4 does not decompose it. Strong HCl breaks it up into $HgCl_2$ and HCy. When SH_2 is passed through its aqueous solution it is decomposed into HgS and HCy.

The alkali ferro- and ferri-cyanides are partially decomposed by warming with dilute sulphuric acid, with evolution of hydrocyanic acid.

This furnishes a convenient method for preparing a solution of hydrocyanic acid. Ten parts by weight of K_4FeCy_6 (yellow prussiate of potash) are distilled in a flask or retort with 36 to 40 parts of dilute sulphuric acid (one of acid to six of water). The flask or retort is connected with a Liebig's condenser and double-necked receiver, from which any uncondensed gas can be carried under a Bunsen lamp, and burnt. Every joint should be made perfectly tight, and the condenser tube should dip into the water placed in the receiver. The reaction takes place according to the equation :
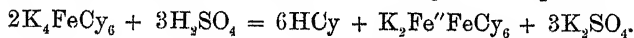
$2K_4FeCy_6 + 3H_2SO_4 = 6HCy + K_2Fe''FeCy_6 + 3K_2SO_4$.
White residue,
turning blue by exposure
to the atmosphere.

That is, only half the cyanogen is given off as HCN.

* $FeCy_2$ is scarcely known in an isolated condition, as it forms in the presence of KCy potassium ferrocyanide, K_4FeCy_6, containing the compound cyanogen radical $FeCy_6$, which in its turn reacts upon the ferric salt.

A solution of HCy, in water or alcohol, when left to itself, undergoes spontaneous decomposition, with production of ammonium formate,* &c. HCN combines also with acids, as HCl, and some anhydrous chlorides. The compounds are mostly easily decomposed even by water. A mere trace of mineral acid retards this decomposition considerably.

Hydrocyanic acid is exceedingly poisonous. Small quantities of the gaseous acid, when inhaled, cause a peculiar sensation in the throat, and are followed by headache, giddiness, and other disagreeable symptoms. Great care must therefore be taken in operating with HCy, or with cyanogen compounds generally, and for the purposes of analysis small quantities only should be operated upon at a time.

HYDROFERROCYANIC ACID, H_4FeCy_6.—This acid is tetra-basic. The potassium salt is prepared on a manufacturing scale by introducing nitrogenous animal substances (horn shavings, &c.) and iron into fused crude potash. The fused mass is lixiviated with water, and the salt allowed to crystallise out. It may also be prepared by decomposing Prussian blue with KHO or K_2CO_3, fused or strong boiling solutions, and separating the ferric hydroxide by filtration, thus : $Fe_4(FeCy_6)_3 + 12KHO = 3K_4FeCy_6 + 2Fe_2(HO)_6$.

Potassium ferrocyanide, $K_4FeCy_6 + 3Aq$, crystallises in large lemon-yellow crystals; hence its name, yellow prussiate of potash. Its positive element (potassium) can, by double decomposition, be replaced by other metals, either entirely or partially, and the property of cyanogen to form double cyanides is well illustrated by the reactions of the ferrocyanides. This will be seen from the following list of some of the more common of these :

K_4FeCy_6	+	3Aq.	$K_2CaFeCy_6$ + 3Aq.	
Na_4FeCy_6	+	6Aq.	Cu_2FeCy_6 + 4Aq.	
$(NH_4)_4FeCy_6$	+	3Aq.	$K_2CuFeCy_6$ + 2Aq.	
Ba_2FeCy_6	+	6Aq.	$K_2FeFeCy_6$.	
$K_2BaFeCy_6$	+	3Aq.	NaK_3FeCy_6 + 3Aq.	
Ca_2FeCy_6	+	12Aq.	$NH_4K_3FeCy_6$ + 3Aq.	
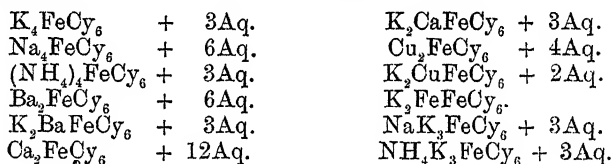
Dry Reactions.

K_4FeCy_6 fuses when strongly ignited, and breaks up into nitrogen, potassium cyanide, and carbide of iron, or a mixture of carbon and iron, thus : $K_4FeCy_6 = 4KCy + 2C + Fe + N_2$.

Heated with free access of air, or in contact with metallic oxides, the KCy is further converted into potassium cyanate, KOCy.

Reactions in Solution.

A solution of potassium ferrocyanide may be used.

The alkali ferrocyanides are readily soluble in water, the alkaline

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* Ammonium formate, NH_4O_2CH, when dehydrated, gives :

    1st, $NH_4O_2CH - H_2O = NH_2OCH$ = formamide, and
    2nd, $NH_2OCH - H_2O = NCH$ = formimide.

This is the reverse reaction.

earthy ferrocyanides are difficultly soluble; those of iron and most other metals are insoluble in water, and many of them are also insoluble in acids. They are decomposed on boiling with potassium hydroxide, with formation of a solution of potassium ferrocyanide and an insoluble metallic hydroxide. Some ferrocyanides are remarkable for characteristic colours, notably so those of iron and copper; others are white, *e.g.*, those of the alkaline earthy metals, of Zn, Pb, Ag, Hg; greenish white, Ni_2FeCy_6, reddish white, Co_2FeCy_6; Mn_3FeCy_6. Potassium ferrocyanide is employed, on this account, as a useful reagent in the qualitative examination of metals, and is especially useful in the detection of iron and copper.

$AgNO_3$ produces a white precipitate of silver ferrocyanide, Ag_4FeCy_6, insoluble in dilute nitric acid and ammonium hydroxide, soluble in potassium cyanide.

$CuSO_4$, added in excess, to a solution of K_4FeCy_6, gives a red chocolate-coloured precipitate of cupric ferrocyanide, Cu_2FeCy_6, whilst an insufficient amount of the cupric salt gives a brown precipitate of dipotassium cupric ferrocyanide, $K_2CuFeCy_6$.

$FeSO_4$ gives a light blue precipitate of potassium ferrous ferrocyanide, $K_2FeFeCy_6$, thus: $K_4FeCy_6 + FeSO_4 = K_2FeFeCy_6 + K_2SO_4$, which is slowly oxidised by exposure to the air, or rapidly, by oxidising agents, such as nitric acid, or chlorine water, to dark blue Prussian blue.

Potassium ferrocyanide is, in fact, readily converted into potassium ferricyanide, $K_6Fe_2Cy_{12}$ (analogous to the conversion of ferrous salts into ferric salts), by various oxidising agents, such as chlorine, nitric acid, potassium chlorate and hydrochloric acid, &c.

Fe_2Cl_6 gives an intensely blue precipitate of $Fe_4(FeCy_6)_3$, called Prussian blue, thus: $3K_4FeCy_6 + 2Fe_2Cl_6 = Fe_4(FeCy_6)_3 + 12KCl$, which constitutes at once a most characteristic and delicate reaction for ferric salts and for ferrocyanogen (as well as for cyanogen, as has been already shown). This precipitate is insoluble in dilute mineral acids, but dissolves in oxalic acid to a blue liquid (blue ink), and in ammonium tartrate to a violet liquid, also used as an ink. It is decomposed by alkali hydroxides, as well as by calcium, and even more readily and completely by magnesium carbonate (magnesite). On boiling with mercuric oxide, Prussian blue is entirely decomposed into $HgCy_2$ and ferrous and ferric oxides, thus:

$$Fe_4(FeCy_6)_3 + 9HgO = 9HgCy_2 + 3FeO + 2Fe_2O_3.$$
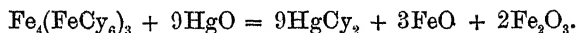
By adding an insufficient amount of Fe_2Cl_6 to a solution of K_4FeCy_6 a blue precipitate is likewise obtained, which is, however, soluble in water, and is therefore called soluble Prussian blue (used for inks). It is generally thought to be composed of Prussian blue combined with potassium ferrocyanide.

Concentrated sulphuric acid (about 10 parts by weight) decomposes potassium ferrocyanide (1 part by weight of the dry salt), with evolution of carbon monoxide (method for preparing carbon

monoxide); the nitrogen of the cyanogen, being converted into ammonia, is retained as ammonium sulphate, thus :

$$K_4FeCy_6 + 6H_2SO_4 + 6OH_2 = 6CO + 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4.$$

All cyanides, except those of silver, are decomposed in the same way.

When concentrated hydrochloric acid is added to an alkali ferrocyanide, hydroferrocyanic acid separates from a cold solution as a white crystalline powder, which turns blue. If ether be added to the solution of potassium ferrocyanide previous to the addition of the acid, it is obtained quite colourless. It is still better when gaseous HCl is passed into the ferrocyanide solution to which the ether has been added.

HYDROFERRICYANIC ACID, H_6FeCy_{12} or H_3FeCy_6.—Potassium ferricyanide is derived from K_4FeCy_6 by a process of oxidation, as, for instance, by passing chlorine into an aqueous solution of it, till a solution of ferric chloride no longer produces a blue precipitate, but imparts merely a brown coloration to the liquid. The change is expressed by the equation : $2K_4FeCy_6 + Cl_2 = K_6Fe_2Cy_{12} + 2KCl$. It is effected by the abstraction of two atoms of potassium from two molecules of K_4FeCy_6. Two atoms of cyanogen are transferred to two molecules of $FeCy_2$, whereby the ferrous cyanide is converted into ferric cyanide.

It is also called red prussiate of potash, on account of its colour.

Reducing agents convert it into potassium ferrocyanide, especially in alkaline solutions.

The following are instances of indirect oxidation effected by potassium ferricyanide :

SH_2 converts the ferri- into ferro-cyanide, with separation of sulphur.
KI   „   „   „   with precipitation of iodine.
Cr_2O_3, or its salts, in the presence of KHO, is converted into CrO_3.
PbO   „   „   „   „ PbO_2.
MnO   „   „   „   „ MnO_2.
SnO   „   „   „   „ SnO_2.
$H_2C_2O_4$ „   „   „   „ $\begin{cases} CO_2 \text{ and} \\ OH_2. \end{cases}$
KCy   „   „   „   „   KOCy.
P_2O_3 „   „   „   „ P_2O_5.
SO_2 „   „   „   „ SO_3.

NH_3 gives with $K_6Fe_2Cy_{12}$ potassium and ammonium ferrocyanides, with evolution of nitrogen, thus :

$$6K_6Fe_2Cy_{12} + 16NH_3 = 9K_4FeCy_6 + 3NH_4FeCy_6 + N_4.$$

Many organic substances, e.g., sugar, dextrine, starch, alcohol, and even paper, are oxidised, in the presence of an alkali, to CO_2 and OH_2. Indigo is bleached. Phosphorus, sulphur, and iodine are converted by the action of $K_6Fe_2Cy_{12}$, in the presence of alkalies, into H_3PO_4, H_2SO_4, HIO_3.

Analogous to potassium ferrocyanide, the ferricyanide forms double ferricyanides, by the partial or entire replacement of the six atoms of the positive element, potassium, by different metals. The following are some of the more important metallic ferricyanides :

$K_6Fe_2Cy_{12}.$ $Ba_2K_2Fe_2Cy_{12} + 3OH_2.$

$Na_6Fe_2Cy_{12} + OH.$ $Fe_3Fe_2Cy_{12}$ (Turnbull's blue).

$Ca_3Fe_2Cy_{12} + 6OH_2.$

Dry Reactions.

Potassium ferricyanide is decomposed upon ignition, yielding cyanogen and nitrogen, and leaving a residue, consisting of potassium cyanide, potassium ferricyanide, Prussian blue, paracyanogen, carbon, and iron.

Reactions in Solution.

A solution of potassium ferricyanide may be used.

The alkali ferricyanides are readily soluble in water. The others are mostly insoluble.

$AgNO_3$ produces an orange-coloured precipitate of silver ferricyanide, $Ag_6Fe_2Cy_{12}$, insoluble in dilute nitric acid, but readily soluble in ammonium hydroxide and potassium cyanide.

$FeSO_4$ gives a blue precipitate (Turnbull's blue) of $Fe_3Fe_2Cy_{12}$, ferrous ferricyanide, which is decomposed by potassium hydroxide into potassium ferrocyanide and ferroso-ferric hydrate or hydroxide:

$$Fe_3Fe_2Cy_{12} + 8KHO = 2K_4FeCy_6 + Fe_3O_4,4OH_2.$$
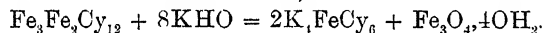
Fe_2Cl_6 produces no precipitate, but gives a brownish coloration. The behaviour of potassium ferro- and ferri-cyanide with iron salts distinguishes between ferrous and ferric salts.

HYDROCOBALTICYANIC ACID, $H_6Co_2Cy_{12}.$—Solutions of cobaltous salts are precipitated by KCy. The precipitate consists of flesh-coloured or cinnamon-brown cobaltous cyanide, $CoCy_2$. Excess of potassium cyanide rapidly dissolves the precipitate, forming a readily decomposable double cyanide, $Co(Cy)_2(KCN)_x$, which on boiling in the presence of HCy is converted into a difficultly decomposable double cyanide, analogous to potassium ferricyanide, with evolution of hydrogen, thus :

$$2Co(CN)_2 + 8KCN + 2H_2O = K_6Co_2(CN)_{12} + 2KHO + H_2.$$
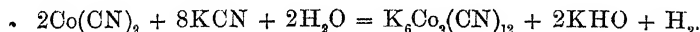
This double cyanide is of interest, as its production affords one means of separating cobalt from nickel, both qualitatively and quantitatively.

The free acid can be obtained from copper cobalticyanide by the action of SH_2. It is soluble in water and alcohol, and is not decomposed by boiling with water or even fuming nitric acid, and dissolves zinc, with evolution of hydrogen.

CYANIC ACID, or Carbimide, HCNO.—Obtained in the form of potassium cyanate by the oxidation of KCy. This salt is very stable when heated by itself, but deliquesces in the air, and is broken up by water into an acid carbonate and ammonia, thus :

$$KOCy + 2OH_2 = HKCO_3 + NH_3.$$
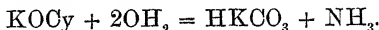
Potassium cyanate is invariably found in commercial potassium cyanide.

Potassium cyanate can be obtained by the oxidation of potassium ferrocyanide in several ways. A simple method is to melt eight parts of dry $K_4Fe(CN)_6$ with three of K_2CO_3, and when the mass is just melted stir in gradually fifteen parts red lead. The mass is kept in fusion and stirred, so that the reduced lead may sink, and the melted KCNO then poured on a plate or tile.

Reactions in Solution.

The cyanates of the alkalies, alkaline earths, and a few metallic oxides are soluble in water, but decompose rapidly, with evolution of ammonia. The silver, lead, mercurous, and cupric cyanates are insoluble in water.

Ammonium cyanate, NH_4CNO, undergoes a molecular change into urea, $CO\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}$, by simply warming its solution.

$AgNO_3$ produces with potassium cyanate a white precipitate of silver cyanate, AgOCy, soluble in ammonium hydroxide, and in dilute nitric acid ; AgCy is insoluble in nitric acid.

Moderately concentrated sulphuric or hydrochloric acid decomposes KOCy, with liberation of HOCy, which affects the eyes most painfully, and is recognised by its pungent odour, resembling that of strong acetic acid ; a portion of the liberated acid is, however, decomposed at once by water into CO_2 and an ammonium salt, thus : $2KOCy + 2H_2SO_4 + 2OH_2 = 2CO_2 + K_2SO_4 + (NH_4)_2SO_4$, and it is by testing for ammonia in the residue from the reaction that the presence of HCyO can be shown under certain conditions. Part of the acid polymerises into cyanuric acid.

A number of cyanates of heavy metals decompose on heating into CO_2 and cyanimide salts—e.g., $Ca(CNO)_2 = CaCN_2 + CO_2$.

SULPHOCYANIC or THIOCYANIC ACID,

SULPHOCYANIC or THIOCYANIC ACID, HSCy, is obtained in combination with potassium by heating KCy with sulphur or a metallic sulphide. Hence the usefulness of potassium cyanide for reducing metallic sulphides in blowpipe reactions. It also combines with sulphur when in solution.

Allyl sulphocyanate is present in mustard seed; the urine of a good many animals contains small but constant amounts of SCN compounds.

CS_2 heated with alcoholic NH_3 solution

$$= CS_2 + 4NH_3 = CNSNH_4 + (NH_4)_2S.$$
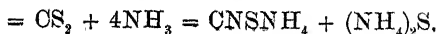
Owing to this method of formation it is found in the ammonia water from coal-gas manufacture.

Sodium amide, $NaNH_2$, is produced by the action of sodium on ammonia gas. This when acted on by CS_2 gives:

$$NaNH_2 + CS_2 = NH_2CSNaS,$$
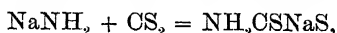
which breaks up into $CNSNa$ and H_2S.

The free acid can be obtained in solution by decomposing $Hg(SCN)_2$ with SH_2. It is a colourless liquid which rapidly decomposes, sometimes explosively. A solution in water also decomposes rapidly unless very dilute. The dilute acid produces a red mark on paper which disappears on warming or after some time.

Warmed with dilute H_2SO_4, a sulphocyanate gives off COS, carbon oxysulphide, and an ammonia salt remains dissolved. Organic acids, as acetic, give an amide, or nitrile, and COS.
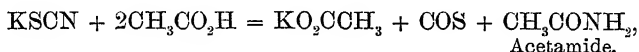
$$KSCN + 2CH_3CO_2H = KO_2CCH_3 + COS + CH_3CONH_2,$$
$$\text{Acetamide.}$$

which again may give $CH_3CN + H_2O$.
$$\text{Acetonitrile.}$$

Chlorine produces from water solutions of sulphocyanates a bright yellow precipitate of $(SCN)_x$, pseudo-sulphocyanogen. $AgCl$ is converted completely into $AgSCN$ on contact with a soluble sulphocyanate, and is consequently the best precipitant for $SCNH$, and is used for quantitative, volumetric, purposes.

Dry Reactions.

$KCyS$ can be fused out of contact with the air without undergoing decomposition. It turns first brown, then green, and lastly indigo-blue, but becomes again colourless on cooling. In contact with the air, $KCyS$ is converted into cyanate and sulphate, with disengagement of SO_2. The sulphocyanates of the heavy metals are decomposed upon ignition, CS_2 being given off at first, and on raising the temperature a mixture of nitrogen and cyanogen is evolved, whilst a metallic sulphide is left:

$$4Cu_2S_2Cy_2 = N_2 + 3C_2N_2 + 2CS_2 + 4CuS.$$
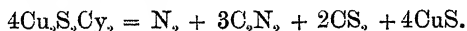
Ammonium sulphocyanate, on heating in a closed vessel, gives some very complex resolution products.

Reactions in Solution.

A solution of ammonium sulphocyanate, NH_4SCN, is used.

$AgNO_3$ produces a white curdy precipitate of silver sulphocyanate, $AgCyS$, insoluble in water and in dilute acids; it is soluble in ammonium hydroxide, from which it crystallises out on evaporation. If the ammonium hydroxide is considerably diluted, the $SCyAg$ will not appreciably dissolve, and $AgCl$ and $AgCy$ may be identified in the presence of $SCyAg$ by this means. It is also soluble in $AmSCy$ or $KSCy$, forming a double sulphocyanate, $SCyAg,SCyK$, from which water or hydrochloric acid precipitates silver sulphocyanate.

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$CuSO_4$ gives a black crystalline precipitate of cupric sulphocyanate, CuS_2Cy_2, which is converted into white cuprous sulphocyanate, $Cu_2S_2Cy_2$, by the action of sulphurous acid.

Fe_2Cl_6 produces an intensely red solution, owing to the formation of a soluble ferric sulphocyanate, $Fe_2(SCN)_6$. Alkali sulphocyanates are most delicate reagents for ferric salts. This reaction serves also for the detection of sulphocyanogen and hydrocyanic acid. The blood-red colour is destroyed by $HgCl_2$. On introducing some metallic zinc into the blood-red solution, SH_2 is evolved.

QUALITATIVE ANALYSIS.—Tabulated Plan.

GENERAL REMARKS.

The student is recommended to most carefully read these general remarks, for by careful attention to the points mentioned the analytical work will be greatly facilitated.

A PRELIMINARY "dry" examination of the substance under analysis should never be omitted before proceeding to the examination for bases in solution.

Apart from the deductions to be drawn from the external properties of the substance, such as its colour, shape, gravity, odour, &c., the detection of certain substances in a preliminary examination will frequently modify the course of analysis to be pursued in solution.

For example, if organic matter has been found by the dry examination, the filtrate from Group II. should be evaporated to dryness, and the residue ignited sufficiently to destroy any such organic compounds as sugar, tartaric or citric acids, which prevent the precipitation of some of the metals in the third group.

But this process of ignition if carried too far renders certain bases insoluble, *e.g.*, Al_2O_3, Fe_2O_3, Cr_2O_3, &c., as well as silica. This would, entail a separate analysis of the residue so obtained. If, therefore, the preliminary examination has established the absence of organic matter, it is better not to ignite here.

If double cyanides have been indicated, it is advisable to ascertain whether there are any present that would interfere with the analysis in the ordinary way.

A reasonable economy in the amount of substance used for analysis should always be observed, and sufficient of the original solid or liquid kept to confirm or to correct doubtful results.

The purity of the reagents used is a point that is too often neglected; alumina is often entered in an analysis because the sodium hydroxide used may have contained it, or iron because fragments of rust from iron apparatus have fallen into the solution. It should also be remembered that ordinary filter-paper is not free from impurities, lime, magnesia, iron, &c.; accordingly, where any pretension is made to strict accuracy, paper that has been carefully washed with dilute hydrochloric and nitric acids should be employed.

The term "addition in excess" is frequently misunderstood by beginners.

It should be remembered that after a sufficient quantity of the reagent has been added any further addition dilutes the solution, and may retard the reaction or commence a re-solution or other secondary reaction.

With properly prepared "normal reagent solutions," equal volumes should complete the reaction in any case, and more is an excess. Generally half as much again may be taken as a fair excess quantity above that actually needed. With normal solutions (see Appendix), say of HCl and NH_3, 1 c.c. of each will just neutralise each other, and $1\frac{1}{2}$ c.c. of HCl would be an excess of the acid.

When preparing a substance for analysis the *smallest possible quantity of acid should be used* to bring it into solution (of course, the solution must be left slightly acid in order to separate the second group). The presence of much strong acid necessitates a considerable dilution with water, evaporation of the greater part of the acid, or a partial neutralisation with ammonia, before the removal of the metals of the second group can be effected. H_2S, for example, completely fails to precipitate Cd if much free acid is present.

Even in working through the separate groups, unless care be exercised, the volume of the liquid becomes inconveniently large, and it is no uncommon occurrence to see beginners working with large beakers half full of liquid, whereas the largest vessel used in an ordinary qualitative analysis ought to be a test-tube or a two-ounce flask, or one of the large test-tubes called boiling tubes.

Evaporation between groups is sometimes advisable, and generally has to be carried out after Group II., before proceeding to the examination for metals in Group III. When soluble silicates or organic matter is present evaporation must be carried to completion.

It is essential in making separations to test a little of each filtrate with more of the reagent which has given a precipitate, otherwise precipitation may be incomplete and cause grave trouble in subsequent operations. This is specially necessary with H_2S in Group II.

The *thorough washing of precipitates* in an analysis must be strictly attended to where indicated, particularly between the groups and subdivisions of the groups, or traces of one group may be retained in the precipitate of the preceding one, causing precipitates to appear in the wrong place, or leading to the appearance of small quantities of other substances when such are not actually present. This *must* be attended to ; many errors arise from neglect of sufficient washing.

Economy in time may be attained by judicious arrangement of an analysis, as many of the operations can be carried on simultaneously.

Care must be taken to label the tube or vessel the contents of which are not to be proceeded with at once.

The student must use his discretion as to the quantity of the sub-

stance or liquid to be taken for the examination of bases in solution, and for this no general rule can be laid down; in substances where comparatively small quantities of one base are expected to be present with large quantities of another, more of the original substance must be taken ; or where the supply at the disposal of the student is large, the trace may be sought for in a separate and larger portion of the original substance, after removal of the bases already detected by the appropriate group agents.

Heavy precipitates entail much washing, an operation which is tedious, but quite indispensable.

Lastly, it is almost unnecessary to remark that strict cleanliness must be observed in all apparatus used for analysis, as there is nothing more annoying than to remember at the end of an analysis, otherwise carefully conducted, in which unexpected results have been obtained, that these may have been due to carelessness in this matter.

All reagent bottles must be replaced immediately after using, and as little loose apparatus permitted on the working bench as possible.

All results, whether positive or negative, must be entered in the note-book *as* obtained, and before passing to the next experiment.

At the end of the exercise the results should always be discussed and the special reactions and tests looked up before making a final report.

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY.

The physical properties of a substance under examination, such as its crystalline structure, its odour, colour, hardness, density, are capable of throwing, in many cases, much light upon its composition, and should be carefully noted.

N.B.—*These reactions are given on the supposition that a "single" substance is under examination; they are, however, still true for a mixture, although not so easy to recognise.*

EXPERIMENT.	OBSERVATIONS.	INFERENCE.	CONFIRMATORY TESTS, &c.
I. Heat a small portion of the substance, in the state of powder, in a small bulb tube or dry test-tube.	THE SUBSTANCE DOES NOT CHANGE	Absence of organic substances, of volatile inorganic matter, of substances decomposed on ignition, of hygroscopic moisture, of water of crystallisation, of readily fusible matters, and of water of hydration (see note, next col.).	*Note.*—As a matter of fact, if the substance be white and does not change it can only be a compound of Al, Ba, Ca, Sr, Mg, and Si with O and a few other substances. Special tests can then be applied (see later).
	THE SUBSTANCE CHANGES		
	1. *The substance changes colour*		
	Yellow whilst hot, white on cooling.	ZnO.	
	From yellow to reddish brown whilst hot, yellow when cold, fusible at a red heat	PbO.	
	From white to yellowish brown when hot, dirty, light yellow on cooling.	SnO_2, [TiO_2.]	
	From white to orange and reddish brown, dull yellow on cooling, fusible at a red heat	Bi_2O_3.	
	Dark red whilst hot, reddish brown on cooling	Fe_2O_3.	

2. *The substance fuses and re-solidifies when the flame is removed*	Mostly salts of the alkalies, and some salts of the alkaline earths (nitrates, chlorides, &c.).	
3. *A sublimate is formed* .	Several compounds of ammonium, antimony, mercury, arsenic, also sulphur and iodine (lead chloride sublimes with difficulty). Metallic cadmium, cadmium chloride, volatile organic acids, *e.g.*, oxalic, benzoic, and succinic acids.	Test specially for ammonium compounds by grinding a little of the original substance in a mortar with soda-lime, and moistening with water.
(a) White sublimate.		
The substance melts at a very gentle heat, heavy fumes appear in the tube, and the sublimate is white and crystalline .	$HgCl_2$	Confirm by heating a little of the dry substance with dry Na_2CO_3, or black flux, in a bulb tube.
It sublimes without previous fusion, is yellow when hot, white when cold .	Hg_2Cl_2	Metallic mirror and globules of metal.
The sublimate consists of white octahedral crystals .	As_2O_3.	Black shining mirror, no metallic globules, As.
The substance fuses into a yellow mass, and at a red heat sublimes entirely forming crystalline needles .	Sb_2O_3.	Bright metallic mirror and brown ring, Cd.
Aromatic odour resembling incense .	Benzoic acid.	
Fumes which cause violent coughing .	Succinic acid. (Oxalic acid.)	
Heavy white fumes, and white crystalline sublimate .	Oxalic acid.	

OBSERVATIONS.	INFERENCE.	CONFIRMATORY TESTS, &c.
(b) Coloured sublimate. The sublimate is black, and turns red on rubbing in the tube or on a paper	HgS	Heated in open ended tube in air SO$_2$ gas given off and metallic globules on cool part of tube.
The sublimate is yellow . . .	HgI$_2$ . . . . . . As$_2$S$_3$	Moistened with HCl and placed on gold coin metal whitened—Hg. Heated open tube odour of arsenic acid and SO$_2$.
Turns pink on rubbing . . . It consists of reddish brown drops, yellow when cold	HgI$_2$. Free sulphur	Sulphides decomposed on ignition blackens silver coin on contact.
Violet vapour, feathery bluish black crystals	Iodine.	
Yellowish and red sublimate, pale green flame at mouth of tube .	Phosphorus.	
4. *The substance fuses, and gives off water of hydration* (sometimes without fusion), or water of *crystallisation,* becoming liquid at a low heat, *i.e.,* it fuses in its water of crystallisation, it then solidifies and fuses again when heated more strongly (igneous fusion), and swells up or intumesces considerably	Metallic hydroxides and salts containing water of crystallisation, *e.g.,* phosphates, borates, alums, and some others.	
(a) Condensed water alkaline to litmus	Ammonium compounds.	
(b) Condensed water acid to litmus .	Free volatile acids, such as HNO$_3$, HCl, H$_2$SO$_4$, H$_2$SO$_3$, &c., or acid salts, organic acids.	
5. *The substance gives off a gas or vapour* *(a) The vapour is colourless and odourless.* Oxygen is given off, causing a glimmering splinter of wood to burst into flame	Metallic peroxides, chlorates, perchlorates, nitrates, bromates, iodates.	*Note.*—Oxygen may be mixed with other gases, *e.g.,* SO$_2$, N, N$_2$O$_4$, Cl, Br, I, from the decomposition of certain sulphates, of nitrates, nitrites, chlorates, hypochlorites, bromates, iodates.
CO$_2$ is given off, which is a non-supporter of combustion, and turns lime-water or baryta-water milky	From the decomposition of carbonates (alkali carbonates excepted); also from the decomposition of oxalates, &c.	*Note.*—(NH$_4$)$_2$CrO$_4$ or (NH$_4$)$_2$Cr$_2$O$_7$ burn in a peculiar manner on gently heating. N gas and steam being given off.
Nitrogen, a non-supporter of combustion; not affecting lime-water	NH$_4$NO$_2$, or some fixed nitrite in the presence of ammonium salts (NH$_4$Cl, &c.), dichromates and ammonium salts.	
ON$_2$, supporting combustion . .	NH$_4$NO$_3$, or some fixed nitrate in the presence of ammonium salts.	
(b) The vapour is colourless, and has characteristic odour SO$_2$ is given off, recognised by its suffocating odour and its acid reaction with litmus paper and bleaching of potassium permanganate or bichromate stain on paper	Acid sulphites; also from the decomposition of sulphates, with or without evolution of oxygen, of earthy sulphites, or thiosulphates; from the action of organic matter upon sulphates, and from the oxidation of metallic sulphides and sulphocyanates.	
SH$_2$, recognised by its odour and action on lead acetate paper	Hydrated sulphides, moist sulphites, and hyposulphites.	

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY—*continued.*

EXPERIMENT.	OBSERVATIONS.	INFERENCE.	CONFIRMATORY TESTS, &c.
	NH_3, possessing a characteristic pungent odour and alkaline reaction to test paper, litmus, or turmeric	From ammonium salts, such as $(NH_4)_2CO_3$, and others containing fixed acids (phosphates, sulphates, borates); from cyanates in the presence of water, and from the decomposition of organic substances containing nitrogen, accompanied by carbonisation and evolution of offensive smelling substances.	*Note.*—Alkali chromates, borates, phosphates, &c., likewise evolve ammonia in the presence of ammonium salts.
	CS_2 is given off . . .	From the decomposition of sulphocyanates.	
	Cl is given off, recognised by its pungent odour. The gas bleaches moistened litmus paper, and is easily recognised by turning starch-iodide papers blue	Several chlorides, such as those of the noble metals Pt, Au; also from certain chlorates and hypochlorites.	*Note.*—Although Cl is coloured, yet in small quantities the colour is so slight as to escape notice.
	(c) *The vapour is coloured, and has characteristic odour.*		*Note.*—All coloured vapours possess odour.
	Reddish brown fumes of N_2O_4 come off, mixed with oxygen	Nitrates of heavy metals, *e.g.*, of Pb, Bi, also certain sulphates in presence of an alkali nitrate.	Paper moistened with α-naphtylamine or diphenylamine sulphate changes to pink or blue. (See "Nitrous Acid.")
	Br and I are given off, recognised by the colour of their vapour, or sublimate, and their action on starch paste	Several bromides and iodides when heated by themselves with exclusion of air, or in the presence of air; in the latter case with formation of oxides, also some bromates and iodates	

II. Heat a little of the substance under examination on charcoal before the blowpipe flame.	Sulphur vapour, which condenses in the upper part of the tube in yellow drops, and burns with a blue flame	From the decomposition of metallic persulphides, e.g.; PtS_2, Au_2S_3, Sb_2S_5, SnS_2, FeS_2, which leave either a lower sulphide or the metal.	Test by contact of vapour with silver coin.
	PH_3 is given off, known by its odour; it sometimes inflames; decolorises permanganate	From the decomposition of certain phosphites, hypophosphites, &c.	
	C_2N_2 is given off, having a peculiar odour, and burning with peach-blossom-coloured flame	From certain compounds of cyanogen.	Paper moistened with $FeSO_4$ and KHO solutions and held in gas turns blue.
	6. The substance becomes carbonised and evolves strongly odorous products of decomposition	From the decomposition of organic animal substances.	Red litmus paper turned blue in gas confirms presence of nitrogen.
	Acetone is evolved, recognised by its characteristic odour	From decomposition of acetates.	
	1. *The substance decrepitates.* Prevent decrepitation by fine powdering or moistening it with water.	NaCl and other crystalline salts.	
	2. *The charcoal burns violently: deflagration*	Nitrates, chlorates, &c.	
	3. *The substance fuses readily, and sinks into the charcoal or forms a liquid bead*	Salts of alkalies, and some salts of alkaline earths, and a few chlorides and bromides.	

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY—*continued.*

EXPERIMENT.	OBSERVATIONS.	INFERENCE.	CONFIRMATORY TESTS, &c.
III. Heat in the inner blow-pipe flame, or in the lower outer edge of a non-luminous flame, on a clean platinum wire.	**1.** *The substance colours the flame* Golden yellow . . . Violet . . . . Yellowish green . . Crimson . . . . Reddish . . . . Green . . . . Blue	Na compounds. K 　　" Ba 　　" Sr and Li compounds. Ca 　　" Cu, B_2O_3, " As, Sb, Pb, $CuCl_2$, $SnCl_2$, $MnCl_2$, $NiCl_2$, and some others also give green or blue-green flames.	*Bead.*　*Incrustation.* Brittle, gives off　White and⎫ white fumes　close to the⎬Sb when withdrawn　substance⎭ from flame Small scattered　Warm brown globules, soft　colour . Cd *Note.*—In the event of a dark residue being obtained on charcoal or a metallic bead, this test should be applied only after removal of metals by H_2S, since Pb, As, &c., attack the platinum wire, and, moreover, may give rise to erroneous conclusions.

Note 1.—A few of the changes observed on heating a substance by itself in a bulb tube occur again when the substance is heated on charcoal, but may be neglected, as they are more readily studied in the tube.

Note 2.—A substance under examination may consist of several bodies, and the reactions which it gives may frequently obscure each other. Moreover, analytical tables cannot possibly provide an explanation for every change that may be produced during the preliminary examination of a mixture of several substances. The student should, therefore, record faithfully every observation he makes, though he may not be able at the time to draw an inference from it, and should endeavour to elicit by further experiments what substances are present in the mixture which he is called upon to examine. Everything should be written down *as soon as* performed. The tabular form here employed is perhaps the shortest and clearest for the purpose. The evidence for and against must then be balanced up.

Note 3.—Graphite and some gas carbons will pass through all these trials without change, as also will some of the platinum group of metals.

EXAMINATION OF AN UNKNOWN SUBSTANCE.

1st. *The substance under examination may be a liquid.*—Examine it by means of well-prepared test-papers. The liquid may be **neutral.**—This excludes a large number of substances, since the greater proportion of normal salts of the metals possess an acid reaction. The liquid gives an **acid** reaction.—This may arise from a free acid, or from the presence of a normal salt having an acid reaction, or from an acid salt.

The solution possesses an **alkaline** reaction—showing the presence of a salt of alkaline reaction, of free alkalies, or alkaline earths, and of cyanides or sulphides of the alkalies or alkaline earthy metals.

Evaporate a portion of the liquid to dryness, on a watch-glass, or platinum foil, and test the vapours evolved with blue and red litmus papers, and also by cautiously smelling them.

If no residue is left, and the vapours have no action on litmus and no odour, the liquid consisted of pure water. Many organic liquids would also evaporate without effect on litmus, but would have a characteristic odour, and frequently are inflammable (alcohol, acetone, &c.).

Acid vapours are evolved—showing the presence of some volatile acid.

Alkaline vapours are evolved.—These will most probably have the characteristic odour of NH_3, arising from either a solution of the gas itself or possibly the decomposition of certain of its salts, such as the sesqui-carbonate, or from amines, such as anilin, &c.

A residue is left.—This will generally consist of salts originally present in solution. Certain salts of organic acids will char, frequently leaving a residue which effervesces with a drop of acid, indicating organic acids in combination with the metals Ba, Sr, Ca, Mg, K, or Na). A sufficient quantity of the residue for examination by the preceding dry tests should be obtained by evaporation.

2nd. *The substance under examination may be a solid.*—If it occur in large pieces, or in the form of a coarse powder, it should first be reduced by mechanical means to as fine a powder as possible.

Natural silicates and compounds which are decomposed with difficulty by acids are finely powdered in an agate mortar and, if necessary, sifted. The coarse particles must then be ground again till the whole of the substance is obtained in an equally fine state of division.

Ascertain whether the solid substance is wholly or in part soluble in water. This is done by boiling about a gram of it in distilled water, allowing the undissolved portion to subside, and evaporating a few drops of the quite clear water to dryness on a watch-glass.

The residue insoluble in water is next treated with dilute hydro-chloric acid, and heated for some time to boiling.

If the substance is not completely dissolved by these means, it is best to take a fresh quantity in a test-tube, pour over it two or three cubic centimetres of concentrated hydrochloric acid, and then to boil until half the acid has evaporated away. Water is added, the contents of the tube are warmed, and if a residue remains it may be treated again in the same way. What fails to dissolve by this method should be regarded as insoluble unless the residue is known by its appearance, or by the preliminary examination, to contain something that would dissolve in aqua regia, $HCl + HNO_3$. In this case, treat the residue with aqua regia, boil off the acids, and add the solution to the hydrochloric solution. Nitric acid or aqua regia should never be used unless it is certainly known that they will be advantageous —*e.g.*, with metals.

The residue insoluble in water and acids should be carefully washed with distilled water, dried, and then mixed with four times its weight of dry Na_2CO_3 and K_2CO_3 (fusion mixture) and fused. The fusion is best performed in a platinum vessel, provided the insoluble residue contains no metals capable of forming alloys with platinum. This can be readily ascertained by an examination of a portion of the residue in the dry way.

It should be borne in mind that only barium and strontium sulphates; silver chloride; SiO_2, and many silicates; native or ignited Al_2O_3 and aluminates; ignited Cr_2O_3 and Fe_2O_3; chrome iron ore; SnO_2 (ignited or as tinstone); ignited Sb_2O_4 (a few metaphosphates and arsenates); CaF_2, and a few other native fluorides; sulphur and carbon, as charcoal or graphites, can be present in the insoluble residue.

Silver compounds in general are changed into $AgCl$ by boiling with aqua regia, and $AgCl$ can be easily removed from an insoluble residue by means of ammonium hydroxide.

The examination of a residue requiring fusion with alkali carbonates is invariably conducted separately. The fused mass is boiled with water and filtered; the part insoluble in water, containing the base in the form of a carbonate (oxide or metal), is dissolved in HCl. The aqueous extract is examined for such acids as would form insoluble compounds with the bases found, as well as for silica.

Alloys should be got into suitable form for solution either by rolling down into foil, drilling, or filing. Some alloys are so brittle that they may be readily powdered. Treat a small portion with a mixture of one part strong nitric acid and one part of water. Should the whole dissolve, Sn and Sb are absent, also Au and Pt.

If a white residue, indicating Sn and Sb, is obtained, the alloy should then be treated with 1 to 1 HCl. Sb is almost completely insoluble in such acid, whilst Sn easily dissolves. If the residue from nitric acid is dark, it may consist merely of small particles of carbon (from the preparation of the alloy), or of finely divided Au or Pt, both of which may be dissolved in aqua regia, $HCl + HNO_3$.

Alloys are best dissolved in a small flask, having a small funnel placed in the neck. Usually a considerable excess of acid has to be employed, and *this must, after solution of the metal, be removed by evaporation.*

Cyanogen compounds are treated of after the tables for the separation of the metals.

As they can all be decomposed by heating to redness in an open dish, the metals previously in combination can be sought for in this ignited residue.

N.B.

REFER TO THESE "NOTES" TO GENERAL TABLE.

(See reference numbers in Table.)

1. If chromium has been indicated in the preliminary examination, and the solution or substance has a yellow or orange colour, make a fresh solution by boiling with a little concentrated HCl and diluting, whether the substance is soluble in water alone or not.

2. If cyanogen has been detected in the preliminary examination, it is advisable to test a portion of the original substance for double cyanides before proceeding in the usual way.

3. If iodine or bromine is present, the solution or substance should be boiled with aqua regia until it is eliminated before passing on to Group II.

4. If the original substance had to be dissolved in HCl, SH_2 may be passed at once.

5. In a saturated solution of a barium or sodium salt HCl produces a white precipitate, which may redissolve in hot water. Such precipitates, however, are never produced in a properly prepared solution. From an alkaline solution HCl may precipitate $Si(HO)_4$ (gelatinous), benzoic and uric acids (crystalline), also Sb_2O_5 (amorphous). Metallic oxides, such as Al_2O_3, and metallic sulphides, such as As_2S_3, Sb_2S_5, Sb_2S_3, SnS, and SnS_2, which dissolve in alkali or ammonium hydroxides, or ammonium sulphide, may likewise be precipitated on the addition of HCl to a solution that is alkaline, and are best examined separately.

6. Oxychlorides of Bi, Sb, or Sn may be precipitated on the first addition of dilute HCl or water, but are readily redissolved on the addition of more acid and gently heating, or the precipitate may be disregarded if the metals of Group I. are absent, since SH_2 readily converts the finely divided oxychlorides into the corresponding metallic sulphides.

7. If arsenic has been detected in the preliminary examination, this filtrate, which may contain pentad arsenic, should be boiled with a solution of sulphurous acid, and the acid solution evaporated considerably to expel the SO_2. Ba, Sr, Pb, when present, may be

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precipitated either partly or wholly as sulphates, and in this case reduction by boiling with alcohol and HCl should be resorted to.

8. SH_2 often produces merely a precipitation of sulphur, owing to the presence of oxidising agents such as Cl, Br, I, H_2SO_3, HNO_2, HNO_3, HClO, $HClO_3$, H_2CrO_4, or ferric salts. This precipitate is easily distinguished by its being white and remaining suspended in the solution. It may be filtered off and neglected. A brick-red precipitate of Pb_2SCl_2 often comes down from strongly acid solutions if they have not been sufficiently diluted with water. Cadmium is very often left in solution if *too much acid* is present.

9. SH_2 should be passed once more through the filtrate to make sure of the complete precipitation of all the metals of Group II., and it is advisable *to dilute a few drops with four or five times their volume of water and again pass SH_2*. If this further dilution enables SH_2 to give more precipitate, the whole solution must be so treated.

10. It is possible that this SiO_2 may be mixed with other substances, *e.g.*, Al_2O_3, Cr_2O_3, Fe_2O_3 (rendered insoluble by strong ignition), $BaSO_4$, $SrSO_4$, in which case it is necessary to examine it separately.

11. If iron is present, the NH_4HO precipitate should be of a good reddish brown colour, but when manganese is present some quantity, in the form of hydrated oxide, accompanies the iron, when the precipitate is distinctly *brownish red*. It is because of the liability of Mn to accompany the $Fe_2(HO)_6$ that the instruction is given to filter quickly. Should Mn have been indicated in the preliminary examination and the precipitate also show indications of its presence, it should be redissolved in HCl, quickly reprecipitated by ammonia, and rapidly filtered, repeating this again if still brownish red. Most (though not all) of the manganese will be found in the filtrate, which should be mixed with the preceding filtrates.

12. Small quantities of borates and fluorides of the alkaline earthy metals may likewise be precipitated, but need not be examined further, since their bases will be detected in Group IV., and their acids on examining in the usual way for acids.

13. If ammonia is present in excess (as is usually the case), or yellow ammonium sulphide is employed, the filtrate will most likely be dark-coloured if Ni is present (*see* p. 143). This is an excellent indication of the presence of Ni. The dissolved NiS may be removed by boiling down the filtrate in a dish before proceeding further.

14. The solution must not be boiled, since the NH_4Cl by double decomposition dissolves the alkaline earthy carbonates, forming chlorides of these metals and ammonium carbonate, which volatilises with the aqueous vapour.

EXAMINATION OF A SOLUTION FOR COMMON BASES.

A SIMPLE GENERAL TABLE FOR SEPARATION OF THE GROUPS.

Do not omit to refer to "Notes" to General Table on p. 321.

Notes 1, 2, 3. To the solution add HCl, as long as a precipitate is produced, and cool the solution if crystals of PbCl₂ appear (**Note 4**).

The PRECIPITATE may contain—

PbCl₂
AgCl
Hg₂Cl₂ (**Notes 5 and 6**).

Examine by Table I.

The FILTRATE (**Note 7**) is saturated with gaseous SH₂, and gently heated (**Notes 8 and 9**).

The PRECIPITATE may contain—

HgS
PbS
Bi₂S₃
CuS
CdS   } In a hydrated form.
SnS
SnS₂
Sb₂S₃
Sb₂S₅
As₂S₃
AuS
PtS₂

Examine by Table II.

Evaporate the FILTRATE till free from SH₂, then add a few drops of concentrated HNO₃, and boil again. (If soluble silicates are suspected evaporate to dryness. If organic matter is present, evaporate to dryness and ignite to destroy it. Moisten the residue in either case with strong HCl, add H₂O, heat and filter off the SiO₂ (**Note 10**), or the carbonaceous matter. Test two or three drops of the solution with an equal bulk of strong HNO₃, and about six times its bulk of (NH₄)₂MoO₄, with gentle warming. A yellow precipitate shows the presence of phosphoric acid.)

To the solution, prepared as may be necessary, add a considerable quantity of NH₄Cl. boil for a few seconds, add NH₄OH, until after boiling up the smell of NH₃ is persistent, and filter at once.

The PRECIPITATE may contain—

Fe₂(OH)₆
Cr₂(OH)₆ } (**Note 11**).
Al₂(OH)₆
And also phosphates of Groups III., IV. and Mg, if they are present. (**Note 12.**)

Examine by Table IIIA. or IIIC.

Pass SH₂ through the FILTRATE and warm.

The PRECIPITATE may contain—

ZnS
MnS   } As hydrated sulphides.
NiS
CoS
(**Note 13.**)

Examine by Table IIIB.

To the FILTRATE add NH₄OH unless it already smells of ammonia, then add ammonium carbonate, and warm gently (**Note 14**).

The PRECIPITATE may contain—

BaCO₃
SrCO₃
CaCO₃

Examine by Table IV.

The FILTRATE may contain—

MgCl₂
KCl
NaCl

Examine by Table V.

TABLE I.—SEPARATION OF THE METAL

Attend most carefully to t

Precipitate may contain PbCl$_2$, AgCl, Hg$_2$Cl$_2$ (Note 1, General Table).

The SOLUTION may contain PbCl$_2$. On cooling white acicular crystals fall out. Confirm by adding solution of K$_2$CrO$_4$. A yellow precipitate indicates PRESENCE OF Pb.	The white RESIDUE may consist of AgCl The SOLUTION may contain AgCl; acidulate with HNO$_3$. A white curdy precipitate indicates PRESENCE OF Ag.

TABLE II.—SEPARATION OF THE METALS O

The precipitate may contain HgS, PbS, Bi$_2$S$_3$, CuS, CdS, SnS, SnS$_2$, Sb$_2$S$_3$, Sb$_2$S$_5$, As$_2$S$_3$. (A the precipitate until free from HCl; boil with sodium hydroxid

RESIDUE.—Wash well and warm for some minutes with HNO$_3$, diluted with its own volume of water, until all action ceases. Dilute and filter.

RESIDUE consists of HgS and S or of S only (F.N. 2). To confirm, dissolve the black residue in a little aqua regia, boil off free chlorine, neutralise with NaHO, acidify with HCl, and introduce a strip of bright metallic copper into the solution. It becomes white or silvered. INDICATES PRESENCE of Hg.	SOLUTION—Add dilute H$_2$SO$_4$ as long as a precipitate is produced cool, add an equal bulk of alcohol (F.N. 3); filter.			
	PRECIPITATE consists of PbSO$_4$. Boil with ammonium acetate and add K$_2$CrO$_4$. Yellow precipitate CONFIRMS Pb.	SOLUTION.—Boil off the alcohol, add excess o NH$_4$OH; boil and filter.		
		The PRECIPITATE consists of Bi(HO)$_3$. Dissolve, off the paper, in a *few* drops of dilute HCl and pour the solution drop by drop into 250 or 300 c.c. water. A white precipitate of BiOCl indicates PRESENCE OF Bi.	The solution, divide into two parts	
			1. If blue, add KCy till colourless and pass SH$_2$. A yellow precipitate of CdS INDICATES PRESENCE OF Cd.	2. Blue colour in cates Cu. Ad acetic acid ti acid, and the K$_4$FeCy$_6$. reddish brow precipitate Cu$_2$FeCy$_6$ INDICATES PRI SENCE OF C

F.N. 1.—CuS is somewhat soluble in (NH$_4$)$_2$S and HgS in SNa$_2$. It is therefore advisable If both CuS and HgS are present dissolve in (NH$_4$)$_2$S, when a little CuS will be found

F.N. 2.—A little PbS may become oxidised and appear with the HgS as PbSO$_4$. It may

F.N. 3.—Do not add the H$_2$SO$_4$ and alcohol unless they are shown to be necessary by givin sold by the Excise authorities gives a precipitate when mixed with water. A n

F.N. 4.—If much Sb be present it may flake off the Pt, but a small number of black float

OF GROUP I. (Precipitated by HCl.)

Footnotes and directions.

. Wash precipitate on filter with hot water till quite free from $PbCl_2$.

Hg_2Cl_2; heat gently with excess of dilute NH_4OH. The RESIDUE is black, consisting of NH_2HgCl. Dissolve in a little aqua regia, nearly neutralise, test the solution with a strip of bright metallic copper. Copper becomes covered with a grey deposit, which becomes silvery when rubbed. Indicates PRESENCE OF Hg.	CAUTION.—Unless HCl be added in excess, and the solution gently heated, oxychlorides of Bi, Sb, as well as Sn (likewise H_4SiO_4, indicated by the formation of a jelly or gelatinous precipitate) and a few other substances, may become precipitated in this group.

GROUP II. (Precipitated by SH_2 in an acid solution.)

and Pt must be tested for specially in a separate portion of the filtrate from Group I.) Wash or ammonium sulphide, or sodium sulphide, and filter (F.N. 1).

SOLUTION may contain As, Sb, Sn (Au and Pt) as sulpho salts. Acidulate with dilute HCl. As_2S_3, Sb_2S_5, and SnS_2 are reprecipitated. Filter and wash; boil with a little concentrated HCl until SH_2 ceases to be evolved, add equal bulk H_2O and filter.

SOLUTION.—Pour into a porcelain dish and put into it a piece of platinum foil with a strip of zinc in contact with it. (*a*) A black stain on Pt indicates Sb. (*b*) A spongy deposit on Zn indicates Sn. Boil the remaining Zn with its adherent Sn, and also any floating particles (F.N. 4), with HCl diluted with its own volume of water. Sb will at most only partly dissolve, whilst all Sn will go into solution, and may be confirmed by adding $HgCl_2$.	RESIDUE contains the As_2S_3 or only sulphur. Confirm As by heating the dried residue with KCy and Na_2CO_3 in a bulb tube. But if $(NH_4)_2S$ has been used, so that there is much sulphur in this residue, the As_2S_3 may be dissolved in a little aqua regia and Reinsch's test applied; that is warmed with clean metallic copper in a test-tube. A grey coating indicates As. This coated Cu when heated in a dry test-tube should give a white crystalline sublimate of As_2O_3.

dissolve the precipitate in the absence of CuS with $(NH_4)_2S$, and in the absence of HgS with SNa_2 the solution.

removed—but this is seldom necessary, by warming the precipitate with ammonium acetate.

precipitate with a few drops of the solution. The "mineralised" spirit now required to be mineralised methylated spirit or rectified spirits should therefore be employed.

particles may arise from the zinc employed containing (Pb),compounds of carbon with iron, &c.)

TABLE IIIA.—SEPARATION OF THE METALS OF GROUP IIIA. PRECIPITATED BY NH$_4$OH.

(*In the absence of Phosphates.*)

The PRECIPITATE consists of Fe$_2$(HO)$_6$, Cr$_2$(HO)$_6$, and Al$_2$(HO)$_6$,[*] precipitated by NH$_4$OH in the presence of NH$_4$Cl. Wash with hot water. Dissolve in dilute HCl, add a solution of NaHO in excess, and *boil* for some time Filter off.

RESIDUE insoluble.—Dry and fuse with fusion mixture and nitre on platinum foil: Boil in water, and filter.

RESIDUE.—Dissolve in dilute HCl, and add K$_4$FeCy$_6$. A precipitate of Prussian blue indicates PRESENCE OF Fe. Test the original HCl solution specially for ferrous and ferric iron by means of K$_4$FeCy$_6$, K$_6$Fe$_2$Cy$_{12}$, or NH$_4$SCN.	SOLUTION yellow. Confirm by adding acetic acid and lead acetate. Yellow precipitate of PbCrO$_4$. PRESENCE OF Cr. *Note.*—Traces of manganese—owing to imperfect separation of Mn from Fe by precipitation with NH$_4$OH and NH$_4$Cl—are indicated by the bluish green colour of the fused mass arising from the formation of an alkali manganate.[*]

SOLUTION. — Add just sufficient litmus solution to distinctly colour the solution, then acidulate with dilute HCl, and add NH$_4$OH in slight excess, or solid NH$_4$Cl may be added, and the solution boiled. A gelatinous precipitate, coloured blue by the litmus, the solution itself being rendered almost colourless, confirms Al.

PRESENCE OF Al.

Note.—If no sodium hydroxide free from alumina can be obtained, it should be made by dissolving a little sodium in alcohol, adding water, and evaporating in a silver or platinum dish until the alcohol has evaporated. Failing silver or platinum a nickel dish is quite safe.

[*] See also Note 11, General Table.

TABLE IIIB.—SEPARATION OF THE METALS OF GROUP IIIB.

(In the absence of Phosphates.) Precipitated by $(NH_4)_2S$ or NH_4OH and SH_2.

One of either of the two following methods may be employed for this separation, both of which are based on the same chemical reactions. Method I. is generally simpler than the second.

METHOD I.

The PRECIPITATE may consist of ZnS, MnS, NiS, CoS (F.N. 1). Wash with water containing a little H_2S, and then quickly pour over the precipitate HCl diluted with ten times its bulk of water.

The SOLUTION contains the Zn and Mn as chlorides. Boil in a dish *till free from* H_2S, add excess NaHO, boil well, and filter (F.N. 2).		RESIDUE (F.N. 3).—Dissolve in HCl and $KClO_3$; thoroughly expel SH_2; nearly neutralise with solid Na_2CO_3; add a solution of KCy, so as just to redissolve the precipitate first produced. Boil briskly for a few minutes, allow to cool (filter off any slight precipitate), and add an equal bulk or more of a strong solution of NaOCl (F.N. 4); warm gently as long as a black precipitate forms, and filter.	
The SOLUTION may contain the Zn as $Zn(ONa)_2$. Pass H_2S. White precipitate confirms Zn. The filter containing the ZnS may be incinerated, and the ash heated on charcoal and moistened with $Co(NO_3)_2$. Green mass confirms Zn.	The RESIDUE turns dark on the paper, indicating Mn. Confirm by burning the paper completely on Pt foil and examining the residue by: (*a*) Borax bead; (*b*) Fusion on Pt foil.		
		PRECIPITATE consists of $Ni_2(HO)_6$. Filter off and confirm by heating a small portion of it on a borax bead before the blowpipe flame. A yellowish to sherry-red bead indicates PRESENCE OF Ni (F.N. 5).	The SOLUTION contains the cobalt as $K_6Co_2Cy_{12}$. Evaporate a small part to dryness and test the residue before the blowpipe flame on a borax bead. A blue bead in both flames indicates PRESENCE OF Co (F.N. 5).

TABLE IIIв. METHOD II.

The PRECIPITATE may consist of ZnS, MnS, NiS, CoS (F.N. 1). Wash off the filter and dissolve the precipitate in dilute HCl, with the addition of a small crystal or two of $KClO_3$ if the precipitate is black. Boil, add NaHO in excess, boil, and filter after allowing to cool a short time (F.N. 2).

| The SOLUTION may contain Zn, as $Zn(NaO)_2$. Add SH_2. White precipitate of ZnS indicates | The INSOLUBLE RESIDUE may contain $Mn(HO)_2$, $Co(HO)_2$, and $Ni(HO)_2$. Wash, dissolve in a little HCl ; nearly neutralise with NH_4OH ; add excess of ammonium acetate ; pass a rapid current of SH_2 for several minutes through the solution and filter. The solution should be acid with acetic acid. | |
| PRESENCE OF Zn (F.N. 5). | The SOLUTION contains the manganese as acetate. Add NH_4Cl, NH_4OH and SH_2. or ammonium sulphide direct to the solution. Flesh-coloured precipitate of MnS indicates

 PRESENCE OF Mn (F.N. 5). | RESIDUE.—Must be examined for Ni and Co as in Method I. |

F.N. 1.—Unless this precipitate is black, Ni and Co need not be looked for. Tests by fusion on Pt foil with fusion mixture, and also on charcoal, moistening with $Co(NO_3)_2$, may in this case be at once applied to a little of the precipitate, in order to identify Mn and Zn.

F.N. 2.—Boiling alkaline solutions are liable to disintegrate the paper of the filter.

F N. 3.—The residue may be advantageously examined on a borax bead. If the bead shows no trace of blue, Co need not be examined for, since mere traces of this metal strongly colour borax, and even in very small quantities will completely mask the nickel coloration.

F.N. 4.—Strong bromine water with NaOH may be used instead of NaOCl A bleaching powder solution may also be used. Also chlorine water.

F.N. 5.—The precipitates should be saved for final confirmatory tests.

TABLE IIIc.—SEPARATION OF THE METALS OF GROUP IIIc. (*When Phosphates are present.*)

Method I.—In most cases the P_2O_5 may be completely removed by mixing the precipitate with tin filings and concentrated HNO_3, allowing the action to go on vigorously in an open dish, evaporating nearly to dryness with repeated stirring, diluting, and filtering from the insoluble metastannic acid, which contains all the P_2O_5. After testing a portion of the diluted filtrate with SH_2, to make sure that it is free from Sn, the filtrate may be examined by Tables III., IV., and for Mg as usual. With care this process is quite perfect.

Method II.—Dissolve the precipitate in dilute HCl, nearly neutralise with solid Na_2CO_3, so that the bulk of the solution may not be increased; add about an equal bulk of a normal solution of sodium acetate and acetic acid, boil for some minutes, and filter hot.

The PRECIPITATE may contain $Fe_2P_2O_8$, $Al_2P_2O_8$, and $Cr_2P_2O_8$, and, if Fe and Al were present in excess of the H_3PO_4, also basic acetates of Fe and Al. Cr does not form a basic acetate.

The precipitate may be examined as usual (Table IIIA.).

To the SOLUTION add Fe_2Cl_6 (F.N. 1), drop by drop, as long as a precipitate forms, and until the colour of the supernatant fluid becomes just red. The remaining phosphates of the alkaline earthy metals are thus decomposed. Dilute with water; digest for some time at a gentle heat by standing the test-tube in a beaker of boiling water; allow to subside, and filter hot. Wash with hot water.

The PRECIPITATE consists of $Fe_2P_2O_8$ and ferric acetate. Neglect.

The SOLUTION contains now only chlorides—possibly of all the metals of Group III. except Fe_2Cl_6, as well as the metals of the alkaline earths, the whole of the phosphoric acid having been eliminated. It should be free from red colour, showing all iron acetate has been thrown down, otherwise, owing to the solubility of $Fe_2P_2O_4$ in ferric acetate, the removal of phosphoric acid will be incomplete. Add NH_4Cl, boil, add NH_4OH, filter quickly.

Precipitate. Examine for Cr and Al according to Table IIIA., the phosphates being eliminated.

Solution. Pass SH_2.

Precipitate.—Examine for Ni, Co, Zn, and Mn, by Table IIIb.

Solution. Add $(NH_4)_2CO_3$.

Precipitate.—Examine for Ba, Sr, and Ca, Table IV.

Solution.—Add sodium hydrogen phosphate, a white precipitate, shows presence of Mg.

F.N. 1.—If Fe_2Cl_6 produces no further precipitate with a portion of the acetic acid solution, it is obvious that no phosphates of the alkaline earthy bases are left, the Fe, Cr, and Al of the original substance being sometimes sufficient to decompose the whole of the phosphates of the alkaline earthy metals in an acetic acid solution into chlorides. In this case no ferric salt need be added to the main portion of the solution.

TABLE IV.—SEPARATION OF THE METALS OF
GROUP IV.

(Precipitated as carbonates by $(NH_4)_2CO_3$.)

The Precipitate consists of Ba, Sr, Ca, as carbonates.   Wash (F.N. 1), dissolve
in hot dilute acetic acid, add K_2CrO_4 (F.N. 2), warm, and filter.

A yellow PRECIPITATE indicates Ba. It is $BaCrO_4$. Wash and dissolve it in dilute HCl and add H_2SO_4; a white precipitate of $BaSO_4$ confirms PRESENCE OF Ba.	To the SOLUTION add $(NH_4)_2SO_4$, or dilute H_2SO_4, and warm the solution for five or six minutes by standing the test-tube in a beaker of boiling water.

A fine granular PRECIPITATE (F.N. 3), which gradually increases, of $SrSO_4$. Confirm by heating on a platinum wire with HCl. A crimson flame, which rapidly fades = PRESENCE OF Sr.	To the SOLUTION add an oxalate or oxalic acid and ammonia. A white precipitate of CaC_2O_4 (F N. 4). Heated on Pt wire, a red flame, persistent for some time, indicates PRESENCE OF Ca.

F.N. 1.—A little of the washed precipitate may be dissolved in a drop or
two of HCl and the flame tested.   It is frequently possible to identify Ba and
either Sr or Ca when present together.   This can be done with certainty by
aid of the spectroscope (see plate, Spectral lines, frontispiece).

F.N. 2.—It is best to try a portion only of the solution with K_2CrO_4, since
if no Ba is present the whole of the solution need not be coloured by the
chromate.

F.N. 3.—If much calcium is present, a copious crystalline precipitate may
come down here.   Such a precipitate, after waiting a few minutes, is filtered
off and warmed with a concentrated solution of $(NH_4)_2SO_4$ and NH_4OH; the
solution so obtained is tested for Ca with ammonium oxalate, and the
insoluble part is tested for Sr.

F.N. 4.—If a perceptible amount of Sr has been allowed to remain in the
solution it will be precipitated here.   It is well to test only a part of the
solution for Ca, and if a small precipitate is produced, which it is supposed
may be due to Sr, to allow the remainder to stand for a longer time, that the
$SrSO_4$ may separate more completely.

Table V.—SEPARATION OF THE METALS OF GROUP V,

(Contained in the filtrate from $(NH_4)_2CO_3$.)

The Solution may contain Mg, K, Na.   Divide it into two parts ($\frac{1}{3}$ and $\frac{2}{3}$).

Smaller Part.	*Larger Part.*
dd HNa_2PO_4, shake, and allow to stand a few minutes. A white precipitate, which may be slow in coming, and if slow will be crystalline and adhere to the sides of the tube, especially if it be stirred with a glass rod, indicates PRESENCE OF Mg.	Evaporate to dryness in a porcelain or platinum dish, and ignite until no more fumes of ammonium salts are evolved. Test the residue on a platinum wire in the flame. If the flame becomes *luminously* yellow PRESENCE OF Na IS INDICATED. The flame is coloured violet— PRESENCE OF K AND ABSENCE OF Na. Look at the flame through blue glass. In any case, dissolve the residue in H_2O with one drop of strong HCl, add about 1 c.c. $PtCl_4$, and evaporate carefully just to dryness. Add alcohol and a little water (F.N. 1). Bright yellow crystalline residue. It is heavy and sinks readily. = PRESENCE OF K.

F.N. 1.—If the residue is whitish yellow and not heavy, add more water or Cl, dilute. This is likely to be the case when sulphates or phosphates are esent in the original substance.

It is well for the student to have a known mixture given for examination containing a few metals, and to be required to separate and confirm not only by these plans, but to be required to construct modified plans of analysis based on the reactions of the metals given in Chaps. IX to XIII.

It will have been noted that no place has been found in the separation tables for some of the non-metallic substances, as carbon, sulphur, phosphorus, &c. These substances are easily found in the preliminary dry examination.

EXAMINATION FOR ACIDS. CAUTIONS.

Before proceeding to the examination for acids, the student will do well to consider carefully which acids can possibly be combined with the bases present. A perusal of the table of Solubility of Salts, given in the Appendix, will materially aid him, and will probably save much labour and time. Some acids are detected on examining for bases—viz., As_2O_3, As_2O_5, SiO_2 and H_3PO_4 in combination with metals of Groups III. and IV.; H_2CrO_4, CO_2, SH_2, H_2SO_3, $H_2S_2O_3$, $ClHO$, HNO_3, the six lastly mentioned acids on dissolving the substance in dilute HCl, or on adding HCl in Group I. The student should be on the look-out for them.

A careful preliminary examination for acids will probably lead to the detection of a further number of acids, e.g., of HI, HIO_3, HBr, $HBrO_3$, and $HClO_3$, HNO_3, HNO_2, HCl, $ClHO$, HF, HCy, H_4FeCy_6, $H_6Fe_2Cy_{12}$, CyOH, and CySH, acetic, oxalic, and other organic acids may likewise be indicated. When more than one of these acids is present, the detection is somewhat more difficult, and the results obtained by a preliminary examination for acids require to be carefully confirmed by the examination of the solution.

Thus, a chloride in the presence of a nitrate, when treated with concentrated H_2SO_4, evolves chlorine and red fumes of lower oxides of nitrogen, and possibly nitrosyl chloride; in the presence of a chromate brownish red fumes of CrO_2Cl_2.

When the preliminary examination gives no distinct indication of the presence of any of the acids just mentioned, H_2SO_4, $B(HO)_3$, H_3PO_4, SiO_2 must be looked for specially. A fluoride with an excess of a borate does not etch glass. The student must bear in mind that acids cannot be detected in quite the same systematic order as bases. and that he ought therefore never to be satisfied till he has confirmed the presence of acids by the most characteristic special tests.

At the same time there is a natural or logical order of procedure. in the case of acids, and the student is strongly urged to study and construct plans of separation and detection of mixed acids. It will be found an extremely valuable exercise.

Remember that in this preliminary examination table the inferences are, in most cases, "indicate" only, not absolute proofs.

Other tests should be applied, and if the student has done some of the experiments under the headings of each of these acids, &c., confirmatory tests will immediately suggest themselves.

PRELIMINARY EXAMINATION FOR ACIDS.

EXPERIMENT.	OBSERVATION.	INFERENCE.	CONFIRMATORY TESTS.
Treat a little of the powdered substance in a test-tube with dilute HCl, and warm gently.	*A colourless and odourless gas is evolved with effervescence*		
	(a) The gas burns, after sufficient has been collected by partially closing the top of the tube with the finger	Hydrogen, liberated from the acid by a free metal—Al, Fe, Mg, Zn, Ni, Sn.	
	(b) The gas turns lime- or baryta-water milky	CO_2 from carbonates, likewise from cyanides and cyanates containing carbonates.	
	A colourless gas with distinctive odour		
	(a) Odour of burning sulphur	SO_2 from sulphites.	*Note.*—SO_2 produces a green colour on paper moistened with a little acidified potassium chromate, due to the reduction of the latter.
	(b) Odour of burning sulphur and free sulphur deposited	From thiosulphates.	
	(c) Fœtid odour, like rotten eggs	H_2S from metallic sulphides.	*Note.*—The gas may be tested with lead acetate paper, which H_2S blackens. Certain sulphides are, however, not decomposed by HCl. (See p. 258.)
	(d) Odour resembles bitter almonds	HCy from cyanides.	
	A coloured gas with distinctive odour		
	(a) Yellowish green gas, suffocating odour	Cl from hypochlorites; also from decomposition of H_2CrO_4 or $K_2Mn_2O_9$ by the HCl.	*Note.*—May be further identified by bleaching litmus and liberating I from KI on a starch-iodide test paper.
	(b) Reddish-brown fumes	N_2O_3 from nitrites.	*Note.*—Nitrous acid also liberates I from KI. Potassium bichromate is also reduced by N_2O_3.

PRELIMINARY EXAMINATION FOR ACIDS—*continued.*

EXPERIMENT.	OBSERVATION.	INFERENCE.	CONFIRMATORY TESTS.
II. Treat a little of the substance with concentrated H_2SO_4, and warm (not sufficiently, however, to volatilise the H_2SO_4). Great care must be taken about this. A temperature very little above that of boiling water is sufficient.	*Certain acids may be given off un-changed, owing to the stronger H_2SO_4 liberating them from their salts*	HCl, HNO_3, HCy, HF, benzoic, suc-cinic, and acetic acids.	Confirm HNO_3 by adding concentrated H_2SO_4 to a portion of the salt and steadily pouring on a solution of $FeSO_4$ in a test tube or adding crys-tals of $FeSO_4$, CH_2O, and then H_2SO_4. Brown ring where liquids meet $HNO_3(HNO_2)$. Distinguish HF by etching on glass or by heating a portion of the original substance with silica and strong H_2SO_4, and hold-ing a wet glass rod in the fumes produced in the tube. The drop of water on the rod is encrusted over from precipita-tion of SiO_2 upon it . . HF
	Decomposition takes place— (a) *Without blackening* .	ClHO and CyOH (already noticed), SH_2, HI, HBr, $ClHO_3$, $HBrO_3$, H_2CrO_4, formic, tartaric, citric, ox-alic, CySH, H_4FeCy_6, $H_6Fe_3Cy_{12}$.	
	SH_2, as well as SO_2 are evolved, owing to the action of reducing agents upon H_2SO_4 .	Metallic sulphides, &c.	

		Heat original substance with strong H_2SO_4 and MnO_2:
Oxygen is given off, and the yellow chromate is changed into green chromic sulphate . . .	H_2CrO_4.	Cl is evolved . . . HCl
Chlorine peroxide, a greenish yellow, highly explosive gas, is given off .	$HClO_3$.	Br ,, . . . HBr
Bromine is evolved (together with HBr and SO_2), which condenses to a reddish brown liquid; the gas colours starch paste yellow .	HBr and $HBrO_3$.	I ,, . . . HI
Iodine is given off; violet fumes and sublimate, colouring starch paste blue . . .	HI.	$Note.$—With the three latter NH_3 is also set free, but at once combines with the H_2SO_4, and hence is not noticed.
Chlorine is evolved . . .	HCl in the presence of chromates, or Mn_2O_3, MnO_2, &c.	Ammonia can then be detected by the action of KHO in a portion of the acid solution.
Chlorine and nitrous fumes are given off . . .	$HClO_3$, together with HNO_3 or HNO_2.	
CO is given off, which does not turn lime-water milky, but burns with a blue flame	Formic acid; also from decomposition of cyanides, ferro- and ferri-cyanides.	
CO and CO_2 are evolved .	Oxalic acid.	
(b) $With\ blackening$		
The substance blackens, owing to separation of carbon, with evolution of CO, CO_2, and SO_2, and gives off the characteristic odour of burnt sugar . . .	Tartaric and citric acids.	

EXAMINATION OF SOLUTION FOR ACIDS.

Before proceeding to this part of the systematic analysis, it is imperative that the student shall carefully consider what acids it is necessary to look for. Some have, perhaps, been indicated as probably present, and there may be other acids that cannot have revealed themselves because of the presence of some interfering constituent. For instance, HCl cannot show in the preliminary examination if HBr is present, because the latter acid gives all the indications that HCl can give. Again, there are a few acids, like H_2SO_4, that give no, or few, preliminary indications of their presence; they must, therefore, always be looked for if it is possible for them to be present.

Having made a list of the acids that are to be searched for, the next matter for consideration is the method of pursuing the search, particularly the preparation of a suitable solution for each test. The practice of *always* preparing the solutions by first boiling with sodium carbonate is not to be recommended.

If the bases present do not interfere, each solution should be prepared by adding the required acid to the aqueous solution, or to the solid substance itself, filtering if necessary. No bases interfere in looking for H_2SO_4 or HCl in a solution.

If bases have to be got rid of (as, for instance, Pb in preparing a solution to test for H_2CrO_4, Ca in a solution for oxalic acid), the solid substance is boiled with a slight excess of Na_2CO_3 solution, the precipitate is filtered off, and those solutions that may happen to be required are prepared in the following way from the filtrate : *

1. Dilute HCl is added to a portion of it, as long as CO_2 is evolved, and till the solution is rendered distinctly acid.

2. Another portion of the alkaline filtrate is rendered acid by means of dilute HNO_3 and boiling.

3. A third portion is rendered acid by means of dilute acetic acid.

4. A fourth portion is carefully neutralised by first adding dilute HNO_3, drop by drop, and boiling as long as CO_2 or other volatile acid is evolved, and till the solution is distinctly acid to test paper ; then by adding a few drops of very dilute ammonium hydroxide till the solution gives a neutral reaction with blue and red litmus papers. The *strictest attention must be paid to these directions*, and the least possible excess of either acid or alkali should be employed, since the precipitation of several acids is prevented by the formation of an ammonium salt in anything like large quantities, on account of the formation of a soluble double salt, *e.g.*, ammonium calcium tartrate, ammonium calcium citrate, &c.

* If a metal is present that must be got rid of, but which Na_2CO_3 will not precipitate, it will be necessary to precipitate it as sulphide from a slightly acid solution. Hg in presence of HCy, Cu and Sb in presence of tartaric acid, &c., are examples requiring this treatment.

If the preliminary examination for bases has shown the presence of ammonium salts, it may be necessary to decompose them by boiling with NaHO solution before preparing Solution ℱ.

Ebullition or fusion with Na_2CO_3 decomposes the phosphates of the alkaline earths but imperfectly; the phosphoric acid so combined is, however, invariably detected by means of ammonium molybdate.

No further notice need be taken of the following acids : CO_2, SH_2, SO_2, HNO_2, $ClHO$, HCy, since they are detected with certainty in the preliminary examination.

1. HCl Solution.

(For H_2SO_4, H_2SiF_6.)

To a Portion of the Solution add $BaCl_2$.

(a) A white precipitate, insoluble on boiling   .   . H_2SO_4

(b) A gelatinous translucent precipitate of BaF_2SiF_4 is obtained. Confirm by drying and heating the precipitate in a tube, when SiF_4 is given off. Take the residue and heat with Na_2CO_3 on charcoal, placed fused mass on silver coin and add 1 drop HCl; brown stain indicates S as H_2SO_4. NH_4OH produces in some solutions gelatinous H_4SiO_4, with formation of NH_4F, BaF_2, and OH_2 .   . H_2SiF_6

To Filtrate, or another Portion, or same Solution if no Result from $BaCl_2$, add Fe_2Cl_6.

(For H_4FeCy_6, $H_6Fe_2Cy_{12}$, HSCy, and H_4SiO_4.)

(a) A deep blue precipitate   .   .   .   . H_4FeCy_6

(b) A brown coloration only. If both acids are present, after adding a slight excess of Fe_2Cl_6, boil and filter off, and observe the colour of the filtrate. If on the addition of SO_2 or $FeSO_4$ to the filtrate a blue precipitate is obtained, it is confirmatory of the presence of $H_6Fe_2Cy_{12}$. Filter again, if necessary   .   .   .   . $H_6Fe_2Cy_{12}$

(c) A blood-red coloration, which is destroyed by $HgCl_2$ and not by HCl (the red colour which acetate imparts to a solution of Fe_2Cl_6 is destroyed by HCl)   .   . HSCy

To a Separate Portion add NH_4Cl or $(NH_4)_2CO_3$.

A gelatinous precipitate, requiring no further confirmation, since SiO_2 is left on evaporating the filtrate from Group II.

H_4SiO_4

2. HNO$_3$ Solution.

(For HCl, HBr, HI, and HCy.)

Add $AgNO_3$.

(a) A white curdy precipitate, very soluble in NH_4HO .   HCl

(b) A yellowish white precipitate, less easily soluble in NH_4HO

HBr

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Confirm by adding Cl water to the original solution and shaking up with chloroform or CS_2. Br colours either solvent a reddish brown.

(c) A yellowish white precipitate, almost insoluble in NH_4HO

HI

Confirm by Cl water and chloroform or CS_2. I colours either solvent violet. The blue compound formed by I with starch may also be used for confirmation.

Detection of HBr in presence of HI.

Add to the solution *one* or *two* drops of chlorine water and shake with chloroform or CS_2. I will be indicated by the usual violet colour. Now cautiously add more Cl water, when the I colour will be destroyed, whilst the Br colour (reddish brown) will become evident. Addition of more Cl water will destroy also the colour due to Br.

Detection of HCl in presence of HBr or HI or both.

To a well-diluted solution in a porcelain dish add dilute H_2SO_4 and then potassium permanganate drop by drop, keeping the solution on the boil. Br and I are liberated. Continue the addition of permanganate until the solution is just permanently pink. Add $AgNO_3$; a white precipitate indicates HCl.

Nitrates may also be tested for in another portion of this solution.

(i) HCy.—*Distinction between HCl, HBr, HI, and HCy.*—Test specially for HCy before proceeding to the examination of the other acids as described, by treating a small quantity of the original substance in a porcelain dish with very dilute H_2SO_4, and causing the evolved HCy to act upon a drop of yellow $(NH_4)_2S$ on filter-paper, contained in a second porcelain dish inverted over the one containing the mixture. The NH_4SCy which is formed gives a blood-red colour upon adding Fe_2Cl_6 if a " single " cyanide was present.

(ii) HSCy ⎫
(iii) H_4FeCy_6 ⎬ are likewise precipitated on the addition of
(iv) $H_6Fe_2Cy_{12}$ ⎭

$AgNO_3$, and are insoluble in dilute HNO_3. The second and third form salts which are insoluble in NH_4OH, whilst AgCy and $Ag_6Fe_2Cy_{12}$ are readily soluble. These acids are, however, best detected in the portion acidulated with HCl.*

· 3. ACETIC ACID SOLUTION.

(For HF, $H_2C_2O_4$, H_2CrO_4, H_3PO_4.)

To a Portion add $CaCl_2$.

(a) A white gelatinous precipitate . . . . . HF

H_2SO_4 may also be precipitated by $CaCl_2$ in a strong

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* No other cyanogen compound but a cyanide gives off HCy when treated with very dilute *centinormal* H_2SO_4, and it is therefore possible also to distinguish HCy in the presence of HSCy, HOCy, H_4FeCy_6, $H_6Fe_2Cy_{12}$.

solution.   HF should, therefore, always be tested for by the etching of glass.

(b) A white precipitate of CaC_2O_4 is obtained, which on ignition leaves $CaCO_3$, soluble with effervescence in acetic acid. (CaF_2 is not affected by ignition)   .   .   . $H_2C_2O_4$

    If the precipitate be a mixture of CaF_2 and CaC_2O_4, after ignition the residue may be examined (a) by dilute HCl for $CaCO_3$, (b) by strong H_2SO_4 and the etching of glass for CaF_2.

To ANOTHER PORTION (or to a portion of the filtrate if $CaCl_2$ gave a precipitate) ADD LEAD ACETATE.

A yellow precipitate of $PbCrO_4$.   .   .   .   . H_2CrO_4

To ANOTHER PORTION ADD Fe_2Cl_6.

A yellowish white, gelatinous precipitate, from a solution of a soluble phosphate or a phosphate decomposable by boiling with Na_2CO_3 .   .   .   . H_3PO_4

Phosphoric acid will, of course, have been found during the examination for bases by the molybdate test.

Arsenic acid, if present, should be first removed by treatment with SH_2.

4. NEUTRAL SOLUTION.

(For the " organic " acids, **Tartaric, Citric, Benzoic, Succinic, Formic, Acetic, Salicylic.**)

To A PORTION ADD $CaCl_2$.

(a) A white precipitate which is crystalline, or becomes so, obtained by vigorously shaking or on standing. *Tartaric acid*

    Treat the precipitate of calcium tartrate, after thoroughly washing, with a strong cold solution of NaHO. After a short time the precipitate dissolves, and on heating it is reprecipitated in a gelatinous form. Characteristic reaction for tartaric acid.

(b) On the addition of $CaCl_2$ in excess, no precipitate is obtained till the solution has been boiled   .   .   .   *Citric acid*

    The precipitate is insoluble in NaHO, but dissolves in NH_4Cl; upon boiling neutral calcium citrate separates again; now no longer soluble in NH_4Cl.

To ANOTHER PORTION ADD Fe_2Cl_6.

(a) A pale yellow precipitate   .   .   .   .   *Benzoic acid*

    Confirm by the reactions which a benzoate gives in the preliminary examination, since a precipitate of $Fe_2(HO)_6$ is frequently mistaken for ferric benzoate, owing to imperfect neutralisation.

(b) A reddish brown precipitate   .   .   .   .   *Succinic acid*

    Separation of Benzoic and Succinic Acids.—Precipitate the two acids with Fe_2Cl_6, warm the washed precipitate

with ammonium hydroxide, filter, concentrate the solution, divide it into two parts, and mix one part with hydrochloric acid, the other with barium chloride and alcohol. Ba succinate precipitates amorphous and almost at once, and benzoic acid forms crystals after some little time.

(c) A red coloration, and on boiling a reddish brown precipitate, similar to that produced by acetic acid . *Formic acid*.

　　If no substance capable of precipitating mercuric chloride be known to be present, heat with $HgCl_2$ to between 60° and 70° and observe if any reduction takes place.

(d) The fluid acquires a deep red colour, owing to the formation of ferric acetate . . . . *Acetic acid*

　　If the solution is nearly neutralised and boiled, the whole of the acetate is precipitated of a reddish brown colour

(e) Purple coloration (very delicate test) . . *Salicylic acid*

It is very essential that with organic acids all possible confirmatory tests, as given in the reactions for the separate acids, should be employed.

SPECIAL EXAMINATION FOR OTHER ACIDS
(Boric, Arsenious, Arsenic).

Boric Acid.—Boric acid is sometimes indicated in the preliminary examination by the swelling up of some of its compounds, and the precipitation of HBO_3 in crystals from a concentrated solution of a borate with moderately dilute H_2SO_4 or HCl. More delicate, however, is the reaction which boric acid gives with turmeric paper, and to the Bunsen flame.

Arsenious and Arsenic Acids.—If As has been found in Group II., some idea as to whether it was present in the arsenious or arsenic solution will have been formed from the manner in which the sulphide is thrown down.

To part of a carefully neutralised solution (ammonium salts may not be present in any quantity)—

1. Add $AgNO_3$.

　　(a) A yellow precipitate, soluble in NH_4HO or dilute HNO_3 . . . . . *Arsenites* or *Phosphates* *

　　(b) A reddish brown precipitate . . . *Arsenates*

2. Add $CuSO_4$.

　　(a) A light green precipitate (Scheele's green, $HCuAsO_3$)
　　　　　　　　　　　　　　　　　　　　　Arsenites

　　(b) A light greenish blue precipitate ($HCuAsO_4$) *Arsenates*

To another solution made alkaline with NH_4HO add magnesia mixture or magnesium sulphate with NH_4Cl; * white crystalline precipitate . . . . . *Arsenates*

* These tests can only be successfully employed when phosphates are known to be absent.

Sulphides which are not easily attacked by acids, or are quite un-attacked.—Mineral sulphides of this type are very commonly met with. Although the artificially prepared sulphide may be readily decomposed by acid, the natural sulphide may be quite unacted on (*e.g.*, lead sulphide and galena, ferrous sulphide and iron pyrites).

Sulphides attacked with difficulty more readily yield H_2S when treated with dilute HCl in presence of finely divided metals, as zinc, aluminium or iron, hydrogen being at the same time evolved.

In general it is better to fuse the finely divided mineral with sodium carbonate, when Na_2S is produced. This may then be treated as a soluble sulphide.

METHOD OF ANALYSIS WHEN CYANOGEN COMPOUNDS ARE PRESENT.

Cyanogen compounds may be of the simple cyanide class, sulpho-cyanides (thiocyanates), or complex cyanides, such as ferro- and ferri-cyanides, cobalticyanides, &c. The presence of cyanogen groups necessitates either their removal, or, if this is impracticable, special methods of analysis, many of the double cyanides being insoluble and difficult to decompose.

Cyanogen compounds will have been indicated by the dry reactions. Simple cyanides will evolve hydrocyanic acid when the dry substance is treated with strong HCl, leaving a solution or residue of metallic chloride, which may be examined as usual. Certain of the double cyanides are also completely decomposed by acids; such cyanides possess an alkaline reaction. (The student is recommended to consult the lists of single and double cyanides on pp. 295, 297.)

AgCN, $Ag_4Fe(CN)_6$, and $Ag_6Fe_2(CN)_{12}$ are decomposable into AgCl by boiling with aqua regia.* Mercuric cyanide (soluble in water) is decomposed by H_2S.

Before commencing the analysis the nature of the cyanogen compound must be ascertained.

(*a*) First ascertain whether the cyanogen compounds are soluble in water; if so, whether the solution is alkaline.

(*b*) Warm with strong HCl. The characteristic blue or green colour of the ferro- or ferri-cyanides may appear in the solution or insoluble residue.

(*c*) Treat a portion of the insoluble residue from HCl with boiling KHO or NaHO, add Na_2CO_3 solution until no further precipitation takes place, boil well, filter, just acidulate the filtrate with dilute HCl, and test for $H_4Fe(CN)_6$ and $H_6Fe_2(CN)_{12}$ by means of ferrous sulphate and ferric chloride (see pp. 300–302).

REMOVAL OF CYANOGEN GROUPS.

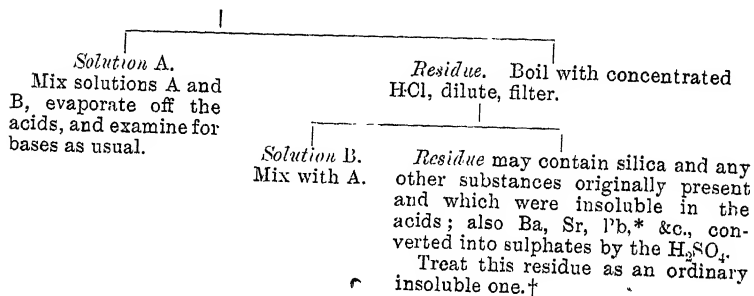The elimination of C_2N_2 from simple and certain double cyanides has been referred to above.

* AgCN is very difficult to decompose. Palladium cyanide is practically undecomposable by any method (strongly heating excepted).

Sulphocyanides may be decomposed by evaporation with strong HNO_3.

Insoluble double cyanides may be decomposed by one of the two following methods, but such a procedure only permits of the metals present being ascertained, and gives no indication of the manner in which they are combined. It is therefore preferable to use the more complete method given later.

Method I.—Fuse the substance in a crucible with either ammonium persulphate or a mixture of ammonium sulphate and nitrate. The ignition should be stopped before all the ammonium salts are volatilised, and the residue may then be examined as usual. Any Ba, Sr, Pb, &c., will be converted into insoluble sulphates.

Method II.—Heat a portion of the substance with pure concentrated H_2SO_4 in a porcelain dish, evaporate off the greater part of the acid, dilute, filter.

Solution A. Mix solutions A and B, evaporate off the acids, and examine for bases as usual.	*Residue.* Boil with concentrated HCl, dilute, filter.

Solution B. Mix with A.	*Residue* may contain silica and any other substances originally present and which were insoluble in the acids; also Ba, Sr, Pb,* &c., converted into sulphates by the H_2SO_4. Treat this residue as an ordinary insoluble one.†

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* Lead sulphate may be wholly or in part converted into the chloride by boiling with strong HCl.

† Test a portion of this residue in the dry way to ensure absence of metals which might alloy with the platinum foil on which fusion is conducted.

METHOD III. This is the more complete method, and, since it indicates the nature of the combinations present, is preferable to the other methods given.

Boil a portion of the original substance with water.

SOLUTION.—Examine in the usual manner for metals (especially the alkalies), and for any acids indicated as possibly present by the preliminary examination.

RESIDUE.—Boil with strong potassium or sodium hydroxide, add a little sodium carbonate, boil again for some time, filter, and wash residue well with hot water.

SOLUTION contains ferro- and ferri-cyanides, and possibly other acids, separated from their bases by boiling with the caustic alkali and carbonate, also those oxides soluble in alkalies—e.g., SiO_2, Al_2O_3, ZnO, PbO, &c.

Pass H_2S until the solution smells strongly of the gas, add a little more KHO or NaHO, heat moderately for a short time, filter, and wash the precipitate.

RESIDUE may contain sulphides of As, Sb, Sn (soluble in the excess of soda), and HgS (soluble in Na_2S), also still certain cyanogen compounds. Acidify with dilute H_2SO_4, filter, and wash.

RESIDUE.—Examine for metals above indicated as usual.

SOLUTION contains $H_4Fe(CN)_6$, $H_6Fe_2(CN)_{12}$, and $H_4Co_2(CN)_{12}$, together with alumina.
Divide the solution and—
(a) Test for hydroferrocyanic acid with Fe_2Cl_6.
(b) Test for hydroferricyanic acid with $FeSO_4$.
(c) Remainder treat according to Method II., and examine for (Fe)Cr, Co, Mn (all of which, if found, were originally present in cyanogen radicals), and Al, which would have been present in basic form.

RESIDUE is now free from cyanogen (unless silver cyanide was present). Dissolve in HCl and examine for bases (including phosphates perhaps), except K or Na.
Ferrous and ferric iron, chromium, cobalt, and manganese may be found in this residue. If so, they were present as the bases of metallic cyanogen acids ($H_4Fe(CN)_6$, &c.), and not a part of the acid radical itself.

RESIDUE may contain HgS, PbS, CuS, ZnS, AgS, &c. Examine by usual methods.

SILICATES.

With the exception of those of potassium and sodium, all silicates are insoluble in water or nearly so.

A few silicates are insoluble in concentrated HCl or H_2SO_4, but the greater number are either partially or entirely decomposed by these acids when heated with them.

Most rocks are mixtures of several silicates, of which some are often decomposable by acids; others are not. If, therefore, it is considered necessary to ascertain, as far as possible, the actual composition of the silicate under examination, it is advisable to examine separately those constituents which show a different behaviour with acids. Silicates such as kaolin and common clays can frequently be decomposed either wholly or partly by concentrated sulphuric acid; many natural silicates yield more or less silica on treatment with hydrochloric acid, which silica may be taken to represent the soluble silica, or the decomposable silicate, leaving the greater portion of the mineral behind in an insoluble condition.

If the ultimate analysis only is required, without reference to how the elements are combined, the silicate may be at once decomposed by fusion with fusion mixture.

In this case the alkalies must be tested for in a separate portion.

Decomposition of Silicates by Fusion with Fusion Mixture.

The silicate is first pulverised very finely in a steel and finally in an agate mortar, then intimately mixed with four or five times its weight of pure fusion mixture, and heated in a platinum crucible as long as any gas is given off. The heating may require to be completed over a powerful blowpipe.

A platinum crucible can be employed with safety only when the absence of easily reducible and fusible metals has been established by a preliminary examination of the siliceous substance in the dry way.

The silica is thus obtained in combination with the alkalies, but there may also be present other acid radicals converted by the fusion into soluble compounds (fluorides and phosphates, for example), also certain oxides originally present in combination as bases with the silicic acid (such as Al_2O_3, Cr_2O_3, Mn_2O_3 or MnO_2, ZnO, SnO_2), which are now in combination as acidic radicles with the alkali bases (aluminates, chromates, &c.). Extraction of the residue with boiling water will remove all the above.

The residue will consist of insoluble carbonates or oxides, and may contain BaO, SrO, CaO, MgO, Fe_2O_3, &c. Chrome iron ore ($FeCr_2O_4$) if originally present will remain unaltered by the fusion, and so will appear in this residue.

Treatment of the Fused Mass.

Repeatedly extract with hot water and filter.

Residue.—Dissolve in hot HCl and examine for all metals (except K and Na) in the usual manner. Any portion insoluble may arise through insufficient powdering and fusion of the substance, or be due to chrome iron ore or TiO_2.* The former may be got into solution, and the metals identified, by treatment with strong HNO_3 and a crystal of potassium chlorate.

Solution.—Divide into two parts.

Part I.—In this it is necessary to decompose the alkali silicates with excess of dilute HCl, and th n render the silica insoluble by evaporation, first gently to avoid spirting, then when the mass is in a pasty condition the temperature is raised, and the mass thoroughly broken up with a glass rod until no large particles remain. This is essential, for if the acid is not completely removed some silica will pass into solution.

Treat the dried mass with a little strong HCl, add water and filter. Any white insoluble residue is SiO_2.

The solution obtained must be examined for metals likely to be rendered soluble by the fusion (Al, Cr, Mn, Zn, Sn).

Part II.—Portions of this should be tested for any acid radicals which in their original combination were insoluble, but owing to the fusion have been converted into soluble sodium or potassium salts. A consideration of the acids which could possibly be present with the bases found will lead to the elimination of many of them.† Parts of the solution may, however, be generally tested with :

(*a*) HCl and barium chloride for *sulphates*.

(*b*) HNO_3 and ammonium molybdate for *arsenates* and *phosphates*. If a precipitate is obtained, then the usual procedure for As must be resorted to, the liquid being afterwards tested for phosphates.

(*c*) HCl in excess, boil off CO_2, add NH_4HO in excess, then $CaCl_2$, and allow to stand. A precipitate indicates *fluorides*, and this precipitate after drying should be confirmed by warming with H_2SO_4 for HF.

(*d*) Acetic acid in excess and lead acetate for *chromates*.

DETECTION OF THE ALKALIES IN ALL SILICATES.

About 1 grm. of the finely pulverised silicate is mixed with 1 grm. of pure powdered ammonium chloride and 8 grms. of pure calcium carbonate. The ingredients are thoroughly mixed in a mortar and introduced into the platinum crucible, which is gently

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* Titanium oxide, if present, will mainly be found in the portion insoluble in boiling water. Its separation from silica is referred to on p. 291.

† If insoluble halogen salts of silver are indicated in the preliminary reactions, then acidify a portion with nitric acid and test for Cl, Br, or I, by $AgNO_3$.

tapped and the contents shaken down tight. The crucible is loosely covered by the lid, and heated to a bright red heat for from forty to sixty minutes.

The crucible is now allowed to cool. When cold the contents will be found to be more or less agglomerated in the form of a semi-fused mass. Tapping with a glass rod will generally detach the mass, which is then to be heated in a beaker with about 60 c.c. of distilled water, when it may slake and crumble after the manner of lime. At the same time water is put into the crucible to slake out any small adhering particles, and this is added to the contents of the other vessel

By this treatment with water the excess of lime used is obtained as a hydroxide, some of the lime is combined with the silica and other ingredients of the silicate in an insoluble form ; and in solution there is the excess of chloride of calcium formed during the reaction, together with the alkalies present in the silicate.

The contents of the vessel are filtered, the residue on the filter is well washed with distilled water, and the washings added to the main solution. The residue is neglected.

Solution.—Precipitate the lime with a solution of pure ammonium carbonate, filter and wash, evaporate the solution on the water-bath to about 40 c.c., when a little more of the carbonate and ammonium hydroxide should be added to precipitate the small amount of calcium which has previously escaped precipitation. Filter through a small filter, wash, and evaporate to dryness on a water-bath, preferably in a platinum dish.

When dry, the dish is very gently heated by a Bunsen flame to drive off the ammonium chloride. Gradually increase the heat until a little below redness. Nothing now but the pure alkali chlorides should remain.

Test the residue in the usual way for potassium and sodium or lithium, and with a spectroscope if possible.

This process may be followed as a quantitative one to obtain the collective alkalies from a silicate.

EXAMPLE OF METHOD OF RECORDING WORK.

The following example is given to illustrate a systematic method of recording the experiments performed, but it also serves to illustrate the fact that in all analytical work the results are arrived at by a systematic process of elimination. Students too often overlook the important point that much information is often obtainable from an apparently negative observation, and every deduction possible from any experiment or observation should be recorded.

EXAMINATION OF A MIXTURE.

PRELIMINARY DRY EXAMINATION.

Compound given : A dirty white powder. Probable absence of oxides and sulphides of heavy metals, Cu, Fe, Cr, Ni, Co compounds, permanganates, chromates.

EXPERIMENT.	OBSERVATION.	INFERENCE.
Gently heated in a bulb tube.	Substance first fused. Then heavy white fumes formed, which condensed in the upper part of the tube .	Probably compounds of NH_3, Hg, As, &c.
Heated stronger.	Gave off reddish brown fumes and a gas which supported combustion. The residue was yellowish whilst hot, dirty white on cooling	Nitrates of heavy metals. Lead, tin, or bismuth probably present.
Heated a portion of the substance, mixed with charcoal—soda-lime in tube.	Odour of NH_3, litmus blued, mirror and metallic globules in tube	NH_3 and Hg compounds.
Heated on charcoal in the blowpipe flame.	Substance gave off heavy fumes, and was partly reduced to the metallic state. The metal malleable and marked paper; incrustation yellow .	Pb.
Solubility. from	The substance dissolved partly in water, partly in HCl, to a colourless solution	Absence of Hg_2Cl_2, AgCl, AgBr, AgI, SnO_2, ignited Al_2O_3, Cr_2O_3, $PbSO_4$, $BaSO_4$, $SrSO_4$, $CaSO_4$, insoluble silicates.
	CO_2 was evolved, which turned lime-water milky	Presence of *carbonate.*
	No odour of H_2S, SO_2, or HCN . . .	Absence of sulphides, sulphites, and cyanides.
	No brown fumes . .	Absence of nitrites.

EXAMINATION IN SOLUTION FOR BASES.

On mixing the water and HCl solutions, acicular needles fell out; probably lead as chloride. Filtered.

CRYSTALS. — Dissolved in hot water, added K₂CrO₄. Yellow precipitate confirms LEAD.

SOLUTION. — Added few drops more HCl (to ensure all PbCl₂ being thrown down), warmed, and passed H₂S. Filtered.

- Black precipitate. Presence of Hg, Cu, Bi, Sn, Pb, possibly also As, Sb, Cd.
  See A.

- Evaporated till free from H₂S, added few drops HNO₃, continued boiling. Part tested with ammonium molybdate. Phosphates absent.

  Evaporated other part to dryness, moistened with HCl, and tested flame. Reddish yellow, like Ca. Then added water. No insoluble residue. Absence of SiO₂.

  Added NH₄Cl and NH₄HO.

  - Passed H₂S.
    - No precipitate. Absence of Fe, Cr, Al.
    - No precipitate. Absence of Zn, Mn, Ni, Co.

      Added (NH₄)₂CO₃. Filtered.
      - White precipitate. Presence of Ba, Sr, Ca. See B.
      - SOLUTION. — Evaporated to dryness, ignited. No residue. Absence of Mg, K, Na.

A.—Examination of H_2S Precipitate.

Thoroughly washed the precipitate and warmed with NaHO.   Filtered.

RESIDUE.—Warmed with 1 to 1 HNO_3 for some time ; diluted, filtered.			SOLUTION.—Added dilute HCl till just acid. No precipitate. Absence of As, Sb, Sn.
RESIDUE.—Black, probably HgS. Dried ; ignited in a bulb tube with dry Na_2CO_3. Metallic globules confirms MERCURY.	SOLUTION.—Is colourless. Cu probably absent. Added dilute H_2SO_4 and alcohol. Warmed, filtered.		
	PRECIPITATE.—White —probably $PbSO_4$. Warmed with ammonium acetate, added K_2CrO_4. Yellow precipitate confirms LEAD.	SOLUTION.— Boiled off spirit, added NH_4HO. No blue colour— Absence of Cu. No precipitate— Absence of Bi.	
		Passed H_2S. No yellow precipitate. Absence of Cd.	

B.—Examination of Ammonium Carbonate Precipitate.

Portion of the washed precipitate dissolved in drop of HCl and flame tested.
Reddish yellow.   Absence of Ba and probably Sr.

Dissolved precipitate in acetic acid and added K_2CrO_4 to part.		
No precipitate. Absence of Ba.	Other portion.—Added ammonium sulphate, and allowed tube to stand for ten minutes in boiling water.	
	No precipitate. Absence of Sr.	Solution.—Added ammonium oxalate A white precipitate—Ca present.

PRELIMINARY EXAMINATION FOR ACIDS.

A carbonate has already been indicated by effervescence with HCl.

EXPERIMENT.	OBSERVATION.	INFERENCE.
Treated with concentrated H_2SO_4.	Cl and nitrous fumes; bleaches litmus-paper; test-tube not etched .	HCl and HNO_3. Absence of HF.
Warmed with MnO_2 and strong H_2SO_4.	Cl evolved . . . No Br or I . . .	HCl. Absence of HBr, HI.
Heated with Cu and strong H_2SO_4.	Brown nitrous fumes .	Presence of HNO_3.
Confirm HNO_3 by means of H_2SO_4 and $FeSO_4$.	A brown ring formed .	HNO_3.

EXAMINATION OF SOLUTION FOR ACIDS.

Dissolved in dilute HCl and filtered.	Dissolved in dilute HNO_3 and filtered.
Added $BaCl_2$. No precipitate. H_2SO_4 absent.	Added $AgNO_3$. White curdy precipitate, soluble in AmHO. Presence of HCl.
This was hardly likely, as Pb was present in a soluble form.	Warmed original substance with MnO_2 and H_2SO_4. Yellow gas $=$ Cl.

Ammonium molybdate, no results: absence of P_2O_5. Moistened with strong H_2SO_4 and alcohol added and inflamed; no yellow-green flame: absence of B_2O_3.

Found—Bases : Hg, Pb, Ca, NH_3.
Acids : CO_2, HNO_3, HCl.

Analytical Group.	Metal.	Compound Heated in Dry Tube.	Moistened with HCl and Heated on Platinum Wire.	Heated in Borax Bead in Blowpipe Flame.	
		Residue is :	*Flame is coloured :*	*Outer flame.*	*Inner flame.*
I.	Pb	Red, hot ; yellow, cold ; fusible.	Bluish.	Nothing marked.	
	Ag	Brownish, hot ; metallic, cold.	—	,,	,,
	Hg	Sublimate of metal.*	—	,,	,,
II. α	Bi	Yellow, cold ; infusible.	Bluish.	—	
	Cu	Black, hot and cold, infusible.	Green.	Light blue.	Red.
	Cd	Brown, hot ; lighter, cold, infusible.*	—	Nothing marked.	
II. β	As	Sublimate.*	Pale blue, thin.	,,	,,
	Sb	,,	,, denser.	,,	,,
	Sn	Yellow, hot ; paler, cold, infusible.	,, streaky.	,,	,,
III. α	Fe	Dark red.	—	Red, hot ; pale yellow, cold.	Pale green.
	Al	White.	—	—	
	Cr	Green or purple.	—	Green.	Green.
III. β	Mn	Black or dark red.	Greenish yellow.	Amethyst.	Colourless.
	Zn	White.	Thin, streaky green.	—	
	Ni	Black.	—	Violet or reddish.	Greyish.
	Co	,,	—	Deep blue (sapphire).	Deep blue.
IV.	Ba	White.	Yellow-green.	—	
	Sr	,,	Crimson-red.	—	
	Ca	,,	Pale red.	—	
V. α	Mg	White.	—	—	
	K	,, fusible.§	Violet.	—	
	Na	,, ,, §	Yellow.	—	
V. β	NH$_4$	Sublimate.*	—	—	

Heated on Charcoal.		Heated with Na$_2$CO$_3$ on Charcoal.‡	Fused on Platinum Foil with Na$_2$CO$_3$ and KNO$_3$.	Remarks and Notes.
Metallic bead. and	*Incrustation.*	*Bead or Residue.*		I.
White, soft.	Yellow.	White, soft, marks paper.	—	* Sublimate is treated with SH$_2$ by passing the gas into tube.
White.	None.	White, malleable	—	Hg becomes black.
. .	. .	. . .	. . .	Cd } " { light As } " { yellow.
White, brittle.	Yellow.	White, brittle, very fusible.	—	Sb " orange. NH$_4$ unchanged.
Red scales.	—	Red, malleable.	—	II.
Hard to get.	Brown.	White, soft, very fusible.	—	Heated in tube with black flux, Hg gives globules of metal;
Strong odour.	White.	Strong odour.	—	Sb and As give black ring and mirror in tube;
White fumes.	Bluish white.	White, brittle.	—	Cd gives brown ring and bright mirror.
Luminous.†	—	—	—	
Black metallic residue, magnetic.	None.	Black metallic particles, magnetic.	—	† White luminous infusible residues *only* are to be moistened with CoN$_2$O$_6$ solution and again heated, when Al becomes blue.
White luminous residue.†	,,	White residue.	●	Zn " green Mg " pink. Sn " dirty
*Green.	,,	Green or yellow mass.	Yellow mass = K$_2$CrO$_4$.	green.
Black.	,,	Black residue.	Blue-green enamel.	Earthy phosphates and all borates become purple or blue.
White luminous residue.†	White.	White ,,	—	
Black magnetic residue.	None.	Black magnetic residue.	—	‡ The appearances are very similar. If an incrustation is given on charcoal alone it is also given when Na$_2$CO$_3$ is used.
Black magnetic residue.	,,	Black magnetic residue.	—	
White luminous.†	,,	}	—	§ If the acid be colourless.
White luminous.†	,,	} Same, less distinct.	—	
White luminous.†	,,	}	—	
White luminous.†	,,	—	—	
Sinks into charcoal.		—	—	
" " "		—	—	
White fumes.		—	—	

APPENDIX I.

REACTIONS OF THE RARE ELEMENTS.

CERTAIN elements (mostly metallic) were termed "rare" when they occurred in nature, so far as was known, to a limited extent, often being peculiar to a certain class of minerals or a particular locality. The possibility of their technical employment seemed remote. More recent research has, however, shown that many of these substances are far more widely distributed, and in greater quantities, than was supposed. Fresh sources of supply of some of those which within the last few years have been found of value for specific purposes are eagerly sought after. Thus, thorium and cerium for incandescence gas mantles, tungsten and vanadium for special steels, iridium for the tips of gold pens, tantalum for electric lamps, are instances of the common employment of these so-called rare metals at the present time.

It is of much greater importance, therefore, that the student should become familiar with these elements than was formerly the case, but for purposes of study it is still desirable to discuss their reactions in a separate section from the generally recognised common metals, and still to refer to them as "rare" or "rarer" elements.

Some of the heavy metals, possessing very little affinity for oxygen, such as palladium, rhodium, osmium, ruthenium, and iridium, are found native, and associated with platinum and gold. Others are found in combination with oxygen, such as titanium, uranium, tantalum, and niobium; with sulphur or arsenic, such as tungsten or wolfram, molybdenum, vanadium, thallium, indium, and germanium.

The rare elements usually classified among the so-called light metals, having a specific gravity for the most part of less than 5, and yielding insoluble oxides which are mostly specifically heavier than their metals, such as glucinum, zirconium, thorium, cerium, lanthanum, didymium (consisting really of two elements, neodymium and praseodymium*), yttrium, erbium, ytterbium, and scandium, are

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* "Didymium" is still employed in the text, although it must be clearly understood that it refers to the mixture of these two elements. In most methods of separation they are thrown down together, and therefore analytically may be conveniently regarded as an element.

chiefly met with in nature as oxides in combination with silica (sometimes combined with titanic, niobic, and tantalic acids); and, lastly, the metals of the alkali group, whose oxides possess the most pronounced basic character and are soluble in water, such as lithium, rubidium, and caesium, are chiefly met with as salts—carbonates, phosphates, or silicates, sometimes in a soluble condition in sea-water or in mineral springs as chlorides.

Like didymium, it is by no means established that some of the rarer of these substances are incapable of further resolution into simpler bodies. The reactions with precipitants is in many cases so similar that separation of one from the other is a difficult and tedious operation.

It is, of course, not pretended that more than an elementary idea of the treatment of the rare metals or minerals containing them is here given.

The following is the analytical position assigned to these metals by the various group reagents:

Group I. *Precipitated by HCl.*—Tungsten, as tungstic acid; niobium, as niobic acid; thallium, as chloride. (Tantalum, as tantalic acid, and molybdenum, as molybdic acid, are soluble in excess of HCl.)

Group II. *Precipitated by SH_2, from a HCl solution, as sulphides:*

(A) *Insoluble in yellow ammonium sulphide:* Palladium, rhodium, osmium, and ruthenium, and thallium in thallic salts (close resemblance to lead).

(B) *Soluble in yellow ammonium sulphide:* Gold, platinum, iridium, molybdenum, tellurium, selenium, and germanium.

Group III. *Precipitated by NH_4Cl, NH_4OH, and $(NH_4)_2S$:* Uranium, indium, thallium, gallium, as sulphides; glucinum or beryllium, thorium, zirconium, cerium, lanthanum, didymium, yttrium, ytterbium, scandium, erbium, titanium, tantalum, samarium (and columbium), as hydroxides. Vanadium, precipitated as sulphide, on adding HCl to the filtrate.

Group IV. None.
Group V. Lithium, caesium, and rubidium.

METALS OF THE ALKALIES.

The alkali metals, caesium, rubidium (potassium, sodium), and lithium, are remarkable for their highly electro-positive character, the powerfully alkaline nature of their oxides and hydroxides, and the very general solubility of their salts. Caesium appears to be the most highly electro-positive member, whilst lithium shows the

least electro-positive character. They exhibit analogous grada-
tions in their respective combining weights, fusion points, specific
gravity, action upon water, and the solubility of their carbonates,
thus :

	Caesium.	Rubidium.	Potassium.	Sodium.	Lithium.
Atomic weights	132·9	85·5	39·1	23	7
Fusion points .	26°–27°	38·5° C.	62·5° C.	97° C.	180° C.
Specific gravity at 15° C.	1·88	1·516	·865	·97	·59
Action of the metals upon water	Decomposes cold water, the hydrogen becoming inflamed.	Do.	Do.	Do., but does not generally inflame the hydrogen.	Do., but with less violence.
Solubility of the respective carbonates	Cs_2CO_3	Rb_2CO_3	K_2CO_3	Na_2CO_3 Not deliques- cent.	Li_2CO_3 Difficultly soluble in water.

Highly deliquescent, absorbing
water speedily from the air.

The salts of all the alkali metals are isomorphous, and in general
properties rubidium stands between caesium and potassium, whilst
lithium appears to form the connecting link between the alkali
metals and the metals of the alkaline earths. This is shown more
especially by the comparatively insoluble nature of its phosphate
and carbonate.

The metals may be obtained by electrolysis of the fused chlorides
or by the reduction of the oxides by carbon or iron at a high tem-
perature. Metals, oxides and hydroxides are volatile at very high
temperatures.

REACTIONS OF THE RARE METALS OF THE ALKALI GROUP.

CAESIUM, Cs′. Atomic weight, 132·9.—Occurs in very small
quantities in many mineral waters, as chloride, and in a few
minerals (lepidolites) ; in large quantities in the rare felspathic
mineral pollux, found in Elba, said to contain 34 per cent. of
caesium.

Both caesium and rubidium were discovered by Bunsen and
Kirchhoff in 1860, whilst examining spectroscopically the saline
residue left on evaporating large quantities of the Dürkheim mineral
water. The hydroxide, CsHO, is very soluble, both in water and
alcohol, and very strongly alkaline. The carbonate, Cs_2CO_3, resembles
potassium and rubidium carbonate, but is soluble in five parts of
boiling alcohol. (Distinction from K_2CO_3, Na_2CO_3, and Rb_2CO_3,
which are practically insoluble in alcohol.)

Dry Reactions.

When heated on platinum wire, in the inner flame of the blowpipe,
volatile caesium salts impart an intense sky-blue colour to the outer
flame (hence the name of the metal, from *caesius*, sky blue).
When examined with a spectroscope, two intensely sky-blue lines,
Csαλ and Csβλ, close upon the strontium line, Srδλ, are seen

(together with various other less distinctly visible lines in the orange, yellow, and green).

Reactions in Solution.

Any salt will give the reactions.

$PtCl_4$ produces a light yellow crystalline (octahedral) precipitate of the double chloride of caesium and platinum, $2CsCl,PtCl_4$, very difficultly soluble in boiling water—·377 part in 100 of water. The corresponding potassium platinic chloride is dissolved by repeated treatment with boiling water.

Tartaric acid produces a colourless, transparent, crystalline precipitate of hydrogen caesium tartrate, THCs ; about eight times more soluble in water than the corresponding rubidium salt.

RUBIDIUM, Rb′. Atomic weight, 85·5.—Occurs widely diffused in nature. It is met with, although only in very small quantities, in a large number of minerals, in lepidolites and in mineral waters, in most natural deposits of potassium salts, likewise in the ashes of many plants, such as tobacco, coffee, beetroot, &c.* It is white, more easily fusible and convertible into vapour than potassium, and takes fire spontaneously in air. Its oxide, rubidia, Rb_2O, is a powerful base, and its salts, like the corresponding caesium salts, are isomorphous with those of the metal potassium. The hydroxide, RbHO, is strongly alkaline, and very soluble in water and alcohol. The carbonate, Rb_2CO_3, is a deliquescent salt, insoluble in alcohol.

Dry Reactions.

Volatile rubidium salts, when heated on a platinum wire in the inner blowpipe flame, colour the outer flame dark red (hence the name rubidium, from *rubidus*, dark red). When examined spectroscopically, two dark red lines, $Rb\delta\lambda$ and $Rb\gamma\lambda$, on the extreme left of the solar spectrum and close to the potassium line, together with two distinctly violet lines, and several weaker lines in the yellow, readily distinguish rubidium compounds.

Reactions in Solution.

Any salt will give the reactions.

$PtCl_4$ produces a light yellow crystalline (octahedral) precipitate of rubidium platinic chloride, $2RbCl,PtCl_4$, very difficultly soluble in boiling water—·634 in 100 water.

Tartaric acid yields a white precipitate of hydrogen rubidium tartrate, THRb, which is soluble in 10·3 parts of water at 25° C.

Rubidium and caesium resemble potassium, also, in forming isomorphous alums, which differ considerably in their solubility in water. 100 parts of water at 17° C. dissolve 13·5 parts of potassium alum, 2·27 of rubidium, and only ·62 part of the caesium alum.

* It is just possible that the fertility of some soils for certain species of plants may be influenced by the presence of salts of these metals

LITHIUM, Li′. Atomic weight, 7·03.—Appears to be widely diffused in nature, although it is found in quantity only in a few silicates, lithia· mica or lepidolite (2 to 5 per cent. of Li), in petalite and spodumene, and in a few phosphates, such as triphylline, or ferrous [manganous] lithium phosphate, $3Fe_3P_2O_8,Li_3PO_4$ (with 3 to 4 per cent. of Li), and amblygonite (6 to 9 per cent. of Li). It has also been found in many mineral springs—most abundantly as yet in a mineral spring in Cornwall—in sea-water, in the ashes of various kinds of tobacco and other plants, and in some meteorites.

The metal lithium is much less oxidisable than potassium and sodium. It makes a lead-grey streak on paper. When freshly cut it has the colour of silver, but tarnishes quickly on exposure to the air, becoming slightly yellow. It is harder than potassium and sodium, but softer than lead. It floats on rock oil, and is the lightest of all known solids, its specific gravity being only ·59. It decomposes water at the ordinary temperatures, with evolution of hydrogen, forming lithium hydroxide, LiHO, but does not melt, and it ignites in air only far above its melting-point (180° C.). The oxide, OLi_2, is not deliquescent.

Dry Reactions.

Lithium salts are more fusible than potassium or sodium salts, and impart a very distinct carmine-red colour to a non-luminous flame when heated on platinum wire. An excess of potassium salt does not materially interfere with the production of this colour ; but the presence of a small quantity of sodium gives rise to an orange-yellow flame. Lithium phosphate requires to be moistened first with hydrochloric acid ; whilst silicates containing lithia must first be decomposed by means of strong sulphuric acid, or by fusion with calcium sulphate, or by treatment with hydrofluoric acid. By means of the spectroscope the occurrence of very minute traces of lithium may be readily detected by a brilliant crimson band, Li$\alpha\lambda$, between the lines B and C, and sometimes a faint yellow line, if the flame of a good Bunsen burner be employed.

Reactions in Solution.

Use a solution of lithium chloride, LiCl.

$PtCl_4$ produces no precipitate.

HNa_2PO_4 (hydrogen disodium phosphate)—but not the corresponding potassium salt —produces on boiling a white precipitate of lithium phosphate, $2Li_3PO_4 + OH_2$, very little soluble in cold water (250 parts), soluble in HCl, and reprecipitated only, on boiling, after neutralisation with NH_4OH. Addition of a few drops of sodium hydroxide after the phosphate, in order that the solution is distinctly alkaline, makes precipitation more certain.

Lithium carbonate, especially after having been fused, is difficultly soluble in cold water, hence an alkali carbonate yields from concentrated solutions of lithium salts a crystalline precipitate of lithium carbonate, Li_2CO_3 (1 part of the carbonate requires 100 parts

of cold water for its solution, but less of boiling water). It is insoluble in alcohol. When fused for a short time on platinum the metal after washing shows signs of corrosion.

Hydrogen lithium tartrate is soluble in water.

Lithium silicofluoride is almost insoluble.

METHODS FOR COMPLETE SEPARATION OF METALS OF THE ALKALI GROUP.

Before any account is given of methods suitable for the separation of these metals, it will be well to consider briefly those differences on which systems of separation may be based.

1. The chlorides of K and Na are almost insoluble in strong alcohol (95 per cent.), whilst those of Cs, Rb, and Li are fairly soluble.

2. The carbonate of Li is relatively insoluble in water. Cs_2CO_3 is soluble in alcohol, whilst Rb_2CO_3 is insoluble.

3. The platino-chlorides differ remarkably in their solubility in water. Thus 100 parts of boiling water dissolve : K, 5·18 parts ; Rb, 0·634 parts ; and Cs, 0·377 parts. At 10° : K, 0·9 parts ; Rb, 0·154 parts ; Cs, 0·05 parts.

4. Caesium hydrogen tartrate is eight times as soluble in water as the corresponding rubidium salt.

5. Rubidium iron alum is readily soluble in hot water, scarcely soluble in cold, whilst potassium iron alum is very soluble, hot and cold.

The metals should be converted into chlorides, and a dry mass obtained by evaporation, then treated with a drop or two of HCl and strong alcohol.

The residue consists of KCl and NaCl.

The solution contains CsCl, RbCl, LiCl. The alcohol is evaporated off and a strong solution in water precipitated by $PtCl_4$.

The solution contains lithium.

The precipitate may be a mixture of Cs_2PtCl_6 and Rb_2PtCl_6 (together with probably a trace of the K salt).

By extraction with boiling water any K salt can be removed, and on igniting the remaining platinum salts in a current of hydrogen the CsCl and RbCl remaining can be separated from the metallic platinum by hot water. The two chlorides are next converted into carbonates by digestion with Ag_2CO_3. The solution can then be evaporated to dryness, and the Cs_2CO_3 extracted with boiling alcohol, Rb_2CO_3 being insoluble. Or, better, the carbonates may be converted into acid tartrates, by adding to the solution twice as much tartaric acid as is necessary to neutralise it. The two tartrates are separated by fractional crystallisation, hydrogen rubidium tartrate crystallising out first, being about eight times less soluble in water than the corresponding caesium salt. On ignition, the pure tartrate yields

again the carbonate, from which the various salts may then be prepared.

Alternative Method of Separation of Cs from Rb.—$SnCl_4$, added to a solution of the chlorides of Na, K, Li, Rb, and Cs, containing free HCl, forms a heavy white precipitate, consisting of nearly pure caesium stannic chloride, $2CsCl,SnCl_4$. By recrystallisation from a hot hydrochloric acid solution, the crystals are obtained pure. This reaction affords an easy method of detecting caesium in a mixture of the alkali chlorides. A hydrochloric solution of $SbCl_3$ acts similarly, precipitating a crystalline double chloride of $CsCl,SbCl_3$. The precipitate is decomposed by water, but can be washed without decomposition with concentrated HCl. The other alkali chlorides (K, Na, and Rb) are not thus precipitated from moderately dilute solutions.

During any process of detecting and separating the metals of this group the spectroscope will prove at each stage of great service.

REACTIONS OF THE RARE METALS OF GROUP III.

Group III. comprises the rare metals uranium, indium, thallium, beryllium (glucinum), thorium, zirconium, cerium, lanthanum, didymium, titanium, tantalum, niobium (or columbium), yttrium, erbium, terbium, samarium, and vanadium.

As it is extremely difficult to obtain the salts of these metals in a pure state commercially, and as the price charged for them puts them out of the reach of most students, it will be preferable to sketch out briefly how some of their minerals can be made to furnish the several salts.

(A) Rare metals precipitated by the group reagents ammonium chloride, hydroxide, and sulphide, in the form of oxides (hydroxides).

Besides the metals aluminium and chromium, already treated of in the main portion of the book, there are:

GLUCINUM (beryllium), Gl''. Atomic weight, $9 \cdot 1$.—This metal occurs only in a few minerals as a silicate, in phenacite, Gl_2SiO_4, combined with aluminium silicate; in beryl, $Al_2O_3.3SiO_2 + 3(GlO.SiO_2)$, and in smaragdite, in euclase, and some other rare metals, such as leucophane.

The metal is obtained, like the metal aluminium, from its chloride. It is white, and has a specific gravity of $1 \cdot 64$. It resembles zinc and aluminium in dissolving in HCl, as well as KHO, with evolution of hydrogen. In other respects also Gl resembles Al, and doubt existed as to whether its oxide was Gl_2O_3 or GlO. It is now definitely settled that the latter is correct, and the metal is closely allied to Mg. Its oxide (GlO) is a white powder, insoluble in water. It may be prepared by fusing the finely powdered native silicate with four times its weight of fusion mixture, decomposing the mass

with HCl, and evaporating to dryness to separate the SiO_2. From the HCl filtrate both the Al_2O_3 and GlO are precipitated by ammonium hydroxide. On boiling the precipitate, however, for some time with ammonium chloride, NH_3 is evolved, and is dissolved out as chloride, $GlCl_2$, the insoluble $Al_2(HO)_6$ remaining behind. The pure gelatinous hydroxide, $Gl(HO)_2$, can then be precipitated from the filtrate by means of ammonium hydroxide. On ignition it yields the white anhydrous oxide, GlO, of specific gravity 3·08.

Another method is to treat the fused mass with H_2SO_4, remove the SiO_2, and recrystallise the potassium alums thus formed, from water, that of glucinum being much more soluble than the aluminium salt.

From the oxide the salts may be obtained by dissolving in the respective acids. Glucina (beryllia) combines both with acids and bases. Its salts are colourless, and of a sweet, slightly astringent taste; they show an acid reaction.

Dry Reactions.

Glucinum compounds give no characteristic reactions in the dry way. GlO and $Co(NO_3)_2$ yields a grey mass when heated on charcoal.

Reactions in Solution.

Use a solution of glucinum sulphate, $GlSO_4$.

The group reagents NH_4HO and $(NH_4)_2S$, as well as the fixed caustic alkalies and alkaline earthy bases, precipitate glucinum hydroxide, $Gl(HO)_2$ (flocculent), soluble, like $Al_2(HO)_6$, in excess of the fixed alkalies, but not in NH_4OH. On boiling, $Gl(HO)_2$ is almost completely reprecipitated from a dilute NaHO or KHO solution. (Distinction from Al_2O_3.) Like Al_2O_3, it is reprecipitated also on the addition of ammonium chloride.

$(NH_4)_2CO_3$ gives a white precipitate of basic glucinum carbonate, freely soluble in excess, reprecipitated as basic carbonate on boiling. (Distinction from Al_2O_3.)

Na_2CO_3 or K_2CO_3 precipitates likewise white carbonate, soluble only in large excess of the precipitants.

$BaCO_3$ precipitates glucinum completely, even in cold solutions.

Oxalic acid or the oxalates give no precipitate, this being an important distinction between Gl and other metals of the group.

Besides these characteristic reactions may be mentioned the difficultly soluble double sulphate, $K_2SO_4,GlSO_4 + 3OH_2$, which the readily soluble glucinum sulphate forms when mixed with potassium sulphate solution.

Separation of Al_2O_3 from GlO.—Dissolve in HCl; pour slowly, and with continued stirring, into a warm concentrated solution of $(NH_4)_2CO_3$. A precipitate forms, consisting of $Al_2(HO)_6$, the solution containing the glucinum as double carbonate. Neutralise filtrate with HCl; boil, and add NH_4OH. $Gl(HO)_2$ is precipitated.

again the carbonate, from which the various salts may then be prepared.

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> $BaCO_3$ precipitates glucinum completely, even in cold solutions.

Oxalic acid or the oxalates give no precipitate, this being an important distinction between Gl and other metals of the group.

Besides these characteristic reactions may be mentioned the difficultly soluble double sulphate, $K_2SO_4, GlSO_4 + 3OH_2$, which the readily soluble glucinum sulphate forms when mixed with potassium sulphate solution.

Separation of Al_2O_3 from GlO.—Dissolve in HCl; pour slowly, and with continued stirring, into a warm concentrated solution of $(NH_4)_2CO_3$. A precipitate forms, consisting of $Al_2(HO)_6$, the solution containing the glucinum as double carbonate. Neutralise filtrate with HCl; boil, and add NH_4OH. $Gl(HO)_2$ is precipitated.

ZIRCONIUM, Zr^{iv}. Atomic weight, 90·6 ; specific gravity, 4·08. —Found as silicate, chiefly in the rare mineral zircon, $ZrSiO_4$. This silicate is not attacked by acids, and the finely divided substance must be decomposed by fusion at a high temperature with fusion mixture, or, better, with KHO. The mass is extracted with water, evaporated to dryness with HCl, in order to remove SiO_2 and to decompose the insoluble, sandy-looking disodium zirconate, $ZrNa_2O_3$, and is then precipitated with NH_4OH. The element itself has been obtained in white, metallic-looking scales by the decomposition of the double fluoride of potassium and zirconium, $2KF,ZrF_4$, by means of metallic aluminium. The element is also obtained mixed with MgO, on heating ZrO_2 with magnesium powder. The hydroxide is white and voluminous, resembling $Al_2(HO)_6$, but is insoluble in alkalies. It dries up to yellowish, transparent lumps, $Zr(HO)_4$, which dissolve readily in acids. On ignition this hydrate loses its water, and also undergoes a molecular change, when the dioxide, ZrO_2, is no longer soluble in dilute acids.

Zirconic salts, obtained by dissolving the hydroxide in dilute acids, are colourless, and of an astringent taste.

Dry Reactions.

Of all the earthy oxides, ZrO_2 is the only one which remains entirely unaltered when submitted to the action of the oxyhydrogen blowpipe. It gives out a very intense and pure light. Moistened with $Co(NO_3)_2$, and intensely heated, the mass becomes of a dirty violet colour. With borax ZrO_2 yields a colourless glass, which becomes slightly opaque when cold.

Reactions in Solution.

Use a solution of the sulphate, $Zr(SO_4)_2$, or chloride, which may be obtained by heating the oxide with ammonium chloride to a high temperature.

The group reagents $(NH_4)_2S$ or NH_4OH produce a white flocculent precipitate of the hydroxide, $Zr(HO)_4$, insoluble in excess; insoluble also in NaHO or KHO; soluble in dilute mineral and some organic acids if precipitated cold. When precipitated from hot solutions the hydroxide is more insoluble (distinction from Al and Gl).

> KHO or NaHO, same precipitate, insoluble in excess, not dissolved by a boiling solution of NH_4Cl (distinction from Gl).
>
> $(NH_4)_2CO_3$ produces a white flocculent precipitate of a basic carbonate, readily soluble in excess, reprecipitated on boiling (distinction from Al).
>
> K_2CO_3 and Na_2CO_3, same precipitate, redissolving in a large excess of K_2CO_3, especially of $KHCO_3$ (distinction from Al).
>
> $BaCO_3$ gives no precipitate in the cold, and precipitates zirconium salts imperfectly, even on boiling.

Oxalic acid or ammonium oxalate gives a bulky precipitate of zirconium oxalate (distinction from Al and Gl), insoluble in excess, difficultly soluble in HCl, soluble in excess of ammonium oxalate (distinction from Th). The normal zirconium sulphite does not give the characteristic reaction with oxalic acid or ammonium oxalate.

HF produces no precipitate (distinction from Th and Y).

$Na_2S_2O_3$ precipitates zirconium thiosulphate, ZrS_2O_3 (distinction from Y, Er, and didymium). The separation takes place on boiling, even in the presence of 100 parts of water to one of ZrO_2 (distinction from Ce and La).

Zirconium sulphate, $Zn(SO_4)_2$, forms with potassium sulphate an insoluble double sulphate of Zr and K, insoluble in excess of K_2SO_4 (distinction from Al and Gl). When precipitated cold, it dissolves readily in a large proportion of HCl, but is almost insoluble in water and HCl, when the K_2SO_4 is added to a hot solution (distinction from Th and Ce).

Turmeric paper, when dipped into a hydrochloric acid solution of a zirconium salt, acquires a brownish red colour after drying in the water-bath (distinction from Th). But titanic acid—the only other metal whose compounds affects turmeric paper under the same circumstances—colours the paper brown, and its presence may therefore prevent the zirconium from being recognised. If the TiO_2 be, however, first reduced by means of zinc and HCl to the state of sesquichloride—the reduction being marked in the solution by a change of colour to pale violet or blue—it no longer colours turmeric paper, and any change in the colour of the latter is then due to zirconium alone. The reaction requires great care, however, as, on exposure of the paper to air, the Ti_2O_3, passing again to the state of TiO_2, would in its turn colour the turmeric paper, and thus render the observation doubtful.

The oxide, ZrO_2, has been used as a substitute for CaO in the oxyhydrogen light and in other gas lights, on account of its greater durability and power of incandescence.

THORIUM, Th^{iv}. Atomic weight, 232·5.—Found in a few rare minerals only—viz., in thorite (orangite), consisting principally of a hydrated silicate, $ThSiO_4,2OH_2$, in monachite, pyrochlor, and monazite.

Thorium compounds have now become of very great commercial importance, since the oxide forms over 98 per cent. of ordinary incandescence gas mantles. Reference is made later (p. 372) to methods by which thorium compounds are separated from other accompanying elements. It is a very desirable exercise for students to effect its separation from the mixture of oxides obtained from a few mantles.

Thorium forms one oxide, ThO_2, which is quite white, and which when heated emits practically no light. The hydroxide, $Th(OH)_4$, is

insoluble in alkalies, and after ignition only soluble with difficulty in acids. In the moist condition it is readily soluble.

Dry Reactions.

ThO_2, when heated before the blowpipe, remains infusible; it imparts no tinge to the flame, and gives a colourless borax bead. It yields no characteristic reaction with $Co(NO_3)_2$ when heated therewith.

Reactions in Solution.

Thorium sulphate, $Th(SO_4)_2$ may be used.

$(NH_4)_2S$ or NH_4OH (group reagents) precipitates the white gela-
tinous hydroxide, $Th(HO)_4$, insoluble in excess.

KHO or NaHO, same precipitate, insoluble in excess (distinction
from Al and Gl).

Ammonium, potassium, and sodium carbonates precipitate white
basic thorium carbonate, readily soluble in excess of the pre-
cipitants, difficultly soluble in dilute solutions (distinction
from Al). From a solution in $(NH_4)_2CO_3$ thorium carbonate
is reprecipitated, even at $50°$ C.

$BaCO_3$ precipitates thorium salts completely in the cold.

Oxalic acid produces a white precipitate (distinction from Al
and Gl), not soluble in excess nor in dilute mineral acids;
soluble in ammonium acetate, containing free acetic acid
(distinction from Y and Ce).

HF precipitates gelatinous thorium tetrafluoride, ThF_4, which becomes pulverulent after some time; the precipitate is insoluble in water and in HF (distinction from Al, Gl, Zr, and TiO_2).

$Na_2S_2O_3$ precipitates thorium thiosulphate, $Th(S_2O_3)_2$, mixed with sulphur, from neutral or acid solutions. The precipitation is not complete (distinction from Y, Er, and Di).

A boiling concentrated solution of K_2SO_4 precipitates slowly, but completely, the whole of the thorium sulphate as white crystalline insoluble potassio-thorium sulphate, $K_4Th(SO_4)_4 + 2OH_2$, (distinction from Al and Gl), soluble with difficulty in cold, and also in hot water, readily on the addition of some HCl.

K_2CrO_4, preferably to a solution in chromic acid (the bichromates of this and allied metals being very soluble), precipitates on boiling $Th(CrO_4)_2.3H_2O$ as an orange-yellow precipitate. Ce, La, and didy-mium do not readily precipitate, whilst Zr gives a basic chromate.

Boiling sodium acetate precipitates basic thorium acetate, $Th(CH_3CO_2)_2(OH_2)_2$. Zirconium also gives a basic acetate, but not Ce, La, or didymium.

Tartaric acid precipitates a basic tartrate, $C_4H_4O_7.Th(OH)_2$. Zr gives a similar precipitate, but not Ce, La, or didymium.

Potassium azoimide (trinitride), which may be prepared by neutralising a dilute solution of azoimide with KHO, completely pre-cipitates Th on boiling. (Ce, La, and didymium give no precipitate.)

Metanitrobenzoic acid, in solutions free from mineral acids, pre-cipitates Th on boiling as $Th(C_6H_4.NO_2.COO)_4$. Ceric salts, but not

cerous, give a precipitate, and also erbium, but no other members of the rare earth groups.

Water saturated with aniline precipitates from chloride or nitrate solutions thorium hydroxide. Ce, La, didymium, Y, Er give no precipitate.

THE RARE EARTHS.

A group of elements is found in certain rare minerals—cerite, gadolinite, euxenite, samarskite, and a few others. The members of this group exhibit close analogies in chemical behaviour, and are usually termed metals of the rare earths. It is a matter of great difficulty to separate them, and possibly some are not really elements. The members of the group, in the order of their atomic weights, are: Scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr) and neodymium (Nd) (forming *didymium*), samarium (Sa), gadolinium (Gd), erbium (Er), terbium (Tb), and ytterbium (Yb), and some others not yet definitely proved as individuals.

SCANDIUM, Sc'''. Atomic weight, $44 \cdot 1$. — This earth concentrates in the insoluble basic nitrates on the separation of Yb. Its nitrate is next to Yb in difficulty of decomposition by heat, the two earths differing greatly in this respect from Er, Tb, Yt, &c. Yb and Sc may be separated by heating their nitrates, or by precipitation of scandium potassium sulphate by addition of K_2SO_4. $Sc_2(SO_4)_3, 3K_2SO_4$ is quite insoluble, the Yb salt soluble. Sc_2O_3 is white, specific gravity $3 \cdot 864$, and resembles MgO or GlO; it is infusible, and not very soluble in acids.

NH_4OH precipitates $Sc(HO)_3$, insoluble in excess of KHO or NH_4OH. The oxalate is slightly soluble in water, 1 in 1080. Other salts are very similar to those of Yb.

This element is found in a number of rare minerals, as euxenite, samarskite, orangite, &c.

YTTRIUM, Y''' (atomic weight, $89 \cdot 0$; specific gravity, $3 \cdot 8$), and **ERBIUM**, Er''' (atomic weight, 166; specific gravity, $4 \cdot 77$).— These very rare elements are only found in a few minerals, as ytterbite, or gadolinite, orthite, yttrotantalite, and in monazite sand, &c. The metals have never been obtained pure. Yttrium and erbium, and possibly terbium, occur together in nature, and closely resemble the metals of the cerite group. They differ from most other earths in being completely soluble in acids, even after ignition, and from the cerite oxides by not forming an insoluble double sulphate with potassium sulphate. In other respects they exhibit almost the same behaviour with reagents, and can only be approximately separated from each other. Yttrium salts are white. Erbium salts have a more or less bright rose tint, crystallise readily, and possess a sweet,

astringent taste. Anhydrous YCl_3 is not volatile (distinction from chlorides of Al, Gl, and Zr).

> $(NH_4)_2S$ or NH_4OH (group reagents) precipitate the hydroxides, insoluble in excess. Large excess of $(NH_4)_2S$ somewhat prevents the precipitation of yttrium hydroxide.
>
> KHO or NaHO precipitates white hydroxides, $Y(HO)_3$ or $Er(HO)_3$, insoluble in excess (distinction from Al and Gl). The precipitation of yttrium by alkali hydroxides is not prevented by the presence of tartaric acid (distinction from Al, Gl, Th, and Zr), yttrium being slowly but completely precipitated as tartrate. Erbium is not completely precipitated.
>
> K_2CO_3 and Na_2CO_3 precipitate white carbonates, difficultly soluble in excess, more readily soluble in $KHCO_3$ and in NH_4HCO_3 (but not so readily as $GlCO_3$). On boiling the whole of the yttria is deposited (distinction of Y from Al, Gl, Th, Ce, and Di). NH_4Cl decomposes $Y_2(CO_3)_3$, with evolution of NH_3 and CO_2 and formation of YCl_3. Saturated solutions of $Y_2(CO_3)_3$ in $(NH_4)_2CO_3$ or Na_2CO_3 have a tendency to deposit a double carbonate.
>
> $BaCO_3$ produces with erbium salts no precipitate, either cold or when heated ; and yttrium salts are but imperfectly precipitated on heating (distinction of Er and Y from Al, Gl, Th, Ce, La, Di).
>
> Oxalic acid produces a precipitate of white yttrium oxalate, $Y_2(C_2O_4)_3 + 6OH_2$ (distinction of Y from Al and Gl), insoluble in excess, difficultly soluble in dilute HCl, and partially dissolved by boiling with ammonium oxalate. Erbium salts are likewise precipitated as oxalate, $Er_2(C_2O_4)_3 + 6OH_2$, in the form of a light rose-coloured, heavy, sandy powder.
>
> HF precipitates white amorphous hydrated yttrium fluoride, insoluble in water and HF; soluble, before ignition, in mineral acids; decomposed only by strong H_2SO_4. (Distinction of Y from Al, Gl, Zr, and Ti.)

A cold saturated solution of $Y_2(SO_4)_3$ becomes turbid between 30°–40° C., and on boiling is almost entirely precipitated.

$Er_2(SO_4)_3$ forms with K_2SO_4 potassio-erbium sulphate,

$$Er_2(SO_4)_3, K_2SO_4,$$
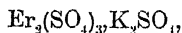
difficultly soluble in cold water when hydrated, but readily soluble in the anhydrous condition, and on warming.

Potassium yttrium sulphate dissolves readily in water and in a solution of K_2SO_4. (Distinction of Y and Er and Sm from Th, Zr, and the metals of the cerite group.)

When erbium nitrate is heated on a platinum wire in a gas flame it imparts an intense greenish colour to the flame, which, when seen through the spectroscope, shows bright lines in the yellow and green, also in the orange and in the blue in an otherwise

continuous spectrum. These bright lines coincide with certain black so-called absorption bands which erbium gives when white light is passed through a concentrated solution of its salts. These absorption bands are characteristic for erbium, as yttrium solutions show none under like circumstances.

In a " radiant matter tube " yttrium compounds give a phosphorescence, the spectrum of which exhibits a number of lines, the most striking of which are in the yellow or orange. Although only present in small amount in any known mineral, Sir W. Crookes' experiments show that yttria is exceedingly widely distributed in nature.

Separation of Y from Er.—The different solubility of the nitrates of erbium and yttrium in water has been made available for the separation of these two closely allied metals. On heating a mixture of their nitrates to incipient decomposition, and dissolving the residue in boiling water, the solution deposits on cooling rose-red crystals of basic erbium nitrate, whilst the mother-liquor contains chiefly yttrium nitrate. By repeating the same process of separation many times the earths may be obtained approximately pure by finally igniting the nitrates.

The only reliable method of separation is to fractionally precipitate and examine each fraction with the spectroscope, or place in a vacuum tube through which an induction charge can be sent, and the phosphorescent glow, given by many substances, examined by the spectroscope.

TERBIUM, Tb. Atomic weight, 139·2.—The oxide, Tb_2O_3, of this metal has been separated from Yt, Er, and Cb in North Carolina samarskite by converting the oxides of Yt, Er, and Tb into formates, and submitting them to fractional crystallisation. The oxide is a dark ochre-brown powder. Its salts are isomorphous with those of white Yt, didymium, and Er.

YTTERBIUM, Yb'''. Atomic weight, 173.—Euxenite is the most abundant source of this earth, where it is accompanied by the oxides of six or seven closely related elements, scandium, samarium, &c. Ytterbia has been separated by the very tedious process of evaporating the nitrates and heating considerably, whereby basic salts insoluble in water are formed, Sc, Th, Di, Er, Y being relatively less soluble than ytterbium. The operations have to be repeated many times. The pure earth is obtained from the nitrate by addition of oxalic acid and igniting the oxalate formed.

Yb_2O_3 is a heavy, white, infusible powder, easily soluble in warm dilute acids. The solutions are colourless. Specific gravity of oxide = 9·175. Its salts have a sweet taste. The nitrate is scarcely decomposed by heating, and remains soluble (characteristic).

NH_4OH precipitates the hydroxide, $Yb(HO)_3$. The sulphate, $Yb_2(SO_4)_3$, is soluble in water. The chloride, $YCl_3.6H_2O$, when dissolved in water, acts on polarised light. The acid selenite, $Yb_2(SeO_3)_3,H_2SeO_3,4OH_2$, is precipitated from neutral solutions, and

is white and insoluble.   The oxalate, $Yb_2(C_2O_4)_3,10OH_2$, is insoluble in dilute acids.

CERIUM, $Ce^{ii, iii}$, and ^{iv}.   Atomic weight, 140·42.   **LANTHANUM,** La'''.   Atomic weight, 138·9.   **PRASEODYMIUM,** Pr^{iii} and ^{iv}. Atomic weight, 140·5.   **NEODYMIUM,** Nd'''.   Atomic weight, 143·6.—These rare metals, with, possibly, samarium, constitute, like Yt, Er, Yb, Sc, and Tb, a group which may conveniently be studied together.   The most abundant of the few cerium minerals is cerite, a hydrated silicate of the three metals Ce, La, and Di, as well as of iron and calcium.   For methods of extraction and separation see p. 372.

CERIUM.   Specific gravity = 7·042.   Melting-point, 623° (?).—This metal exists both in the dyad, pseudo-triad, and tetrad condition. Metallic cerium may be obtained by electrolysing the fused chloride mixed with 10 per cent. of $NaCl + KCl$, using a current of 30–40 ampères at 12–15 volts, also by the aluminium powder reaction.

The metal, heated to 250–270° in a current of hydrogen, burns, forming a *hydride*, CeH_3, stable in dry air; heated in nitrogen to 850°, the *nitride*, CeN, a brass-yellow substance, is formed.

It forms the several oxides :

$$CeO \text{ (?)} \qquad Ce_2O_3 \qquad Ce^{iv}O_2 \quad \text{and} \quad Ce_3O_4 \text{ or } CeO,Ce_2O_3 \text{ (?)}.$$
Cerous oxide. Ceric oxide. Ceric   Ceroso-ceric oxide, or
            (sesquioxide). dioxide.   triceric tetroxide.

Ceric oxide and ceric dioxide are both capable of combining with acids to form two series of salts.   The pure oxides may be insoluble in HNO_3, but in presence of La and didymium *soluble* complex oxides are formed.   They are colourless, or slightly amethyst-red, and acid to litmus.   Cerous chloride is fusible, but not volatile (distinction from Al, Gl, and Zr).   Cerous sulphate is not entirely soluble in boiling water.

Cerous chloride may be formed by rapidly heating a mixture of the oxide with ammonium chloride to about 800° C.

Dry Reactions.

All cerium compounds give with borax, or microcosmic salt, in the outer flame, a clear bead, which is dark red while hot (distinction from the preceding earths), fainter or nearly colourless on cooling. In the inner flame a colourless bead, or, if ceric oxide is present, a yellow opaque bead, is obtained.   Lanthanum compounds give colourless beads, and didymium compounds give with borax colourless, or, if in large quantity, pale rose-coloured beads, in both flames, and with microcosmic salt in the reducing flame an amethyst-red bead, inclining to violet.

Reactions in Solution.

(A) **CEROUS COMPOUNDS.**—A solution of cerous chloride, Ce_2Cl_6, or the nitrate, may be used.

Ammonium sulphide (group reagent) throws down the white cerous hydroxide, $Ce_2(HO)_6$, insoluble in excess. The moist hydroxide absorbs oxygen, becoming purple, then yellow. On ignition ceric oxide results.

Ammonium hydroxide precipitates a basic salt, insoluble in excess; the presence of tartaric acid prevents the precipitation by NH_4HO (distinction from Y), but not by KHO.

Excess of NH_4HO, followed by addition of hydrogen peroxide (H_2O_2), gives an orange precipitate or coloration, affording a very delicate test for Ce.

KHO or NaHO precipitates white cerous hydroxide, insoluble in excess, which turns yellow on exposure to the air, or when acted upon by oxidising agents, such as chlorine water, sodium hypochlorite, &c., being converted into yellow hydrated ceroso-ceric oxide, $Ce_3O_4,3H_2O$ (distinction from Al and Gl).

K_2CO_3, Na_2CO_3, or $(NH_4)_2CO_3$, produces a white precipitate of cerous carbonate, $Ce_2(CO_3)_3$, sparingly soluble in excess of the fixed carbonates, somewhat more soluble in $(NH_4)_2CO_3$; insoluble in water and CO_2; decomposed by dilute acids.

$BaCO_3$ precipitates cerium salts slowly, but completely, on standing.

Oxalic acid, or ammonium oxalate, precipitates cerium compounds completely, even from moderately acid solutions, as a curdy white precipitate (turning slowly crystalline) of cerous oxalate, $Ce_2(C_2O_4)_3,9H_2O$, insoluble in excess of the precipitants (distinction from Zr), but soluble in a large excess of HCl and somewhat soluble in ammonium acetate. On ignition cerous oxalate leaves yellowish white ceroso-ceric oxide, Ce_3O_4, or CeO_2 (distinction from Al and Gl, which form soluble oxalates).

A saturated solution of potassium sulphate produces a white crystalline precipitate of potassio-cerous sulphate, $3K_2SO_4,Ce_2(SO_4)_3$, even from somewhat acid solutions (distinction from Al and Gl); difficultly soluble in cold water, readily soluble on heating, quite insoluble in a saturated solution of K_2SO_4 (distinction from Y and Er); soluble in much dilute HCl. With dilute solutions the precipitates take some time to form.

This characteristic precipitate, as well as the easily distinguishable oxalate, and the yellow precipitate of ceroso-ceric oxide—free from La and didymium, precipitable in the filtrate as oxalates—which oxidising agents produce, serve to distinguish cerium from all other metals.

(B) **CERIC COMPOUNDS.**—Salts of CeO_2, such as the sulphate, oxalate, &c., are yellow, and are either difficultly soluble or insoluble in water. Dyad (triad) (?) cerium appears, in fact, to give rise to more stable compounds; thus, CeO_2, when heated with HCl, does not form $CeCl_4$, but yields $(CeCl_2) + Cl_2$.

Oxidising agents, such as Cl, passed into a solution of KHO,

·containing $Ce_2(HO)_6$ in suspension, sodium hypochlorite, PbO_2, HNO_3, HgO, or potassium permanganate, convert cerous into ceric compounds, and furnish methods for the separation of Ce from La and didymium. Reducing agents produce the reverse chemical action. Cerium resembles in this respect iron rather than aluminium.

LANTHANUM. Specific gravity = 6·154. Melting-point, 810°.— This metal forms only one class of salt, which is colourless when free from didymium salts, and possesses a sweet, astringent taste.

Metallic lanthanum can be obtained by the electrolysis of its fused chloride. When heated in hydrogen to 240° it forms the *hydride,* LaH_3, which is more stable than CeH_3. At a red heat with nitrogen it forms the nitride, LaN.

Lanthanum forms an oxide, La_2O_3, and a peroxide, $La_2O_5 + nH_2O$ (?).

Lanthanum oxide is white, and is not altered even by strong ignition (distinction from Ce), being still readily soluble in acids. Both the oxide and the hydroxide turn red litmus paper blue. By fusing La_2O_3 with alkali carbonates, or heating with concentrated solutions of the hydroxides, lanthanates of the type $M_2.La_4O_7$ are formed. La_2O_3 decomposes ammonium salts, in solution, on boiling, with evolution of NH_3. Lanthanum resembles in this respect magnesium. La_2O_5 slowly evolves oxygen, has basic properties, but does not form compounds with acids, as does La_2O_3. A cold saturated solution of lanthanum sulphate deposits a portion of the salt already at 30° C. (distinction from Ce). In its reactions lanthanum closely resembles cerium.

Reactions in Solution.

Use a solution of lanthanum chloride, $LaCl_3$.

> Ammonium sulphide and hydroxide precipitate basic salts, which pass milky through the filter on washing.
>
> KHO or NaHO precipitates lanthanum hydroxide, $La(HO)_3$, insoluble in excess, unalterable in the air or in the presence of oxidising agents (distinction from Ce).
>
> Ammonium carbonate gives a precipitate which is insoluble in an excess of the precipitant (distinction from Ce).
>
> K_2CO_3, Na_2CO_3, $BaCO_3$, oxalic acid, or potassium sulphate gives similar precipitates as with cerium salts.

When the slimy precipitate which a cold dilute solution of lanthanum oxide yields on supersaturation with ammonia is washed repeatedly with cold water, and a few small crystals of iodine added to it, a blue coloration is produced, which gradually pervades the entire mixture (characteristic for La compounds only).

PRASEODYMIUM, Pr (atomic weight, 140·5; specific gravity, 6·475 melting-point, 940°), and **NEODYMIUM,** Nd (atomic weight, 143·6;

specific gravity, 6·956 ; melting-point, 840°), were regarded as the one element *didymium*, but Welsbach succeeded in resolving the latter into its two constituent elements. Both metals form double sulphates with potassium, that of Nd being the more soluble in solutions of K_2SO_4, hence affording a basis for their separation. The double manganese nitrate, crystallisable from 1·3 sp. gr. nitric acid, also affords a very good method.

Praseodymium forms two oxides—Pr_2O_3, a green substance, from which the salts may be derived, and PrO_2, which is black, does not yield salts, and behaves generally as a peroxide, evolving oxygen when heated strongly and Cl when heated with HCl.

Generally the praseodymium salts are green and give green solutions. Most of them crystallise with several proportions of water of crystallisation. The principal simple salts are : $PrCl_3.7H_2O$, which loses water at ordinary temperatures in dry air, forming $PrCl_3.3H_2O$ (this salt, on heating to 185° in a current of dry HCl gas, yields the anhydrous chloride as a green liquid); the nitrate, $Pr(NO_3)_3.6H_2O$; the sulphate, $Pr_2(SO_4)_3$, with 8 or 5 H_2O ; the oxalate, $Pr_2(C_2O_4)_3.8H_2O$; and the carbonate, $Pr_2(CO_3)_3.8H_2O$.

The chloride forms a double salt with $PtCl_4$—$PrCl_3.PtCl_4.12H_2O$.

Potassium sulphate forms a heavy crystalline precipitate, $Pr_2(SO_4)_3.3K_2SO_4.H_2O$, very sparingly soluble in water.

Neodymium forms an oxide, Nd_2O_3, which is a blue powder, and possibly one of the composition Nd_4O_7—probably a mixture. The salts vary in colour from lilac blue to reddish violet, but the presence of traces of Pr salts somewhat affects the colours.

$NdCl_3.6H_2O$ consists of rose-coloured crystals, which may be rendered anhydrous by heating in a current of dry HCl gas.

The other salts closely resemble those of praseodymium.

By the electrolysis of the fused chloride (56 ampères at 25 volts) the metal is obtained in silvery white form. It decomposes water on warming, and is easily attacked by acids.

Salts of the mixture of praseodymium and neodymium, previously known as *didymium*, give the following reactions :

Ammonium sulphide and hydroxide precipitate a basic salt, insoluble in NH_4OH, but slightly soluble in NH_4Cl, with displacement of NH_3.

KHO or NaHO precipitates a gelatinous hydroxide, resembling $Al_2(HO)_6$, but of a pale rose colour ; it is insoluble in excess, and does not alter in the air.

Alkali carbonates produce a copious precipitate of didymium carbonate, insoluble in excess of the precipitants (distinction from Ce), but slightly soluble in a concentrated solution of NH_4Cl.

$BaCO_3$ precipitates didymium compounds slowly (more slowly than Ce or La), and never completely.

Oxalic acid precipitates didymium salts almost completely; ammonium oxalate completely. The precipitate is difficultly soluble in cold HCl, but dissolves on heating.

A concentrated solution of K_2SO_4, or, better still, Na_2SO_4, precipitates didymium solutions more slowly and less completely than cerous solutions, as a rose-white potassio-didymium sulphate, slightly soluble in water, less soluble in an excess of the reagent, difficultly soluble in hot HCl.

SAMARIUM, Sa. Atomic weight, 150·3.—The oxide, Sa_2O_3, has been obtained from the salt separated by fractional crystallisation of the double magnesium nitrates from nitric acid of 1·3 sp. gr.

The chloride has the formula $SaCl_3.6H_2O$, but when heated to 180° in dry HCl gas $SaCl_3$ is formed.

The nitrate, $Sa(NO_3)_3.6H_2O$, crystallises in thick orange-coloured crystals, which are very hygroscopic. The sulphate has the formula $Sa_2(SO_4)_3.8H_2O$.

GADOLINIUM, Gd. Atomic weight, 156.—Like Sa, this can be separated by fractional crystallisation of the double Mg nitrates. From earths poor in Sa the Gd appears in the last fractions to crystallise. It can be further purified by fractional precipitation with NH_4HO.

Gadolinium oxide, Gd_2O_3, is a white powder easily soluble in water. It absorbs CO_2 from the air.

Gadolinium salts are colourless, give no absorption spectrum, and have an astringent taste.

The chloride, $GdCl_3.6H_2O$, combines with $PtCl_4$, forming orange-yellow needles, $GdCl_3.PtCl_4.10H_2O$.

$Gd(NO_3)_3.5H_2O$ crystallises out from strong HNO_3.

The sulphate, $Gd_2(SO_4)_3.8H_2O$, separates as small crystals, which form a double salt with K_2SO_4 of the composition

$$Gd_2(SO_2)_3.K_2SO_4.2H_2O,$$

the latter being somewhat soluble in saturated K_2SO_4 solution.

SEPARATION OF METALS OF THE RARE EARTHS.

The separation of these metals in anything like a pure state is a very difficult matter. The precipitates obtained must be redissolved and reprecipitated many times, since they generally carry down fair amounts of other metals which it is not desired shall come down. For complete methods students should consult the original papers, but a bare outline of processes is given below.

The silicate must first be decomposed by very finely powdering and heating for a long time with concentrated H_2SO_4, evaporating off the acid, and heating still further.* SiO_2 is thus rendered insoluble; the sulphates produced are dissolved in ice-cold water and precipitated

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* Another method is to mix the finely powdered silicates with sal ammoniac and throw into a red-hot crucible.

as oxalates by oxalic acid, from which the oxides can then be obtained· by ignition.

Glaser recommends fusion of monazite sand with $KHSO_4$, when SiO_2 and tantalum oxide remain insoluble; titanium is thrown down by H_2S, and then the hydroxides obtained by precipitation.

A method due to Fresenius and Hintz for the separation (quantitatively, after obtaining in solution in sulphuric or hydrochloric acid) is as follows :

Boil the well-diluted solution with sodium thiosulphate.

Precipitate is mainly $Th(S_2O_3)_2$.

Well wash and dissolve in dilute HCl (1). Filter from S set free, and ignite this sulphur to obtain oxides it holds, fusing the residue with $KHSO_4$. Dissolve in water, add NH_4HO, filter, dissolve the precipitate in HCl, and mix with the first solution, (1).

The two solutions are largely diluted. and again precipitated with $Na_2S_2O_3$.

Precipitate is pure $Th(S_2O_3)_2$ from which the oxide may be obtained by ignition.

Filtrate.—Add this to (2).

Solution.—Contains other metals, and still some Th (2).

The traces of Th may be removed by another precipitation.

Filtrate when free from thorium is precipitated by NH_4HO, dissolved in nitric acid, evaporated, redissolved in water, and warmed with oxalic acid.

Ce, Y, La, and didymium are precipitated. Heat the oxalates strongly, and fuse with $KHSO_4$ to obtain a solution ; precipitate with NH_4HO, filter, and dissolve in HCl ; nearly neutralise with Na_2CO_3, add excess of acetic acid and then sodium hypochlorite; boil.

Precipitate is CeO_2.

Filtrate.—Evaporate to dryness, add very little water and strong solution of potassium sulphate. Allow to stand several hours.

Precipitate is La and didymium.

Solution contains Y. Add NH_4HO, filter and wash, dissolve in HNO_3, and precipitate with NH_4HO as $Y(HO)_3$.

La and didymium may be identified by adding KHO to their solution until no absorption bands are given by the clear solution. Didymium is precipitated together with some La, but the solution can be obtained free from didymium.

Many methods rely upon fractional crystallisation more than on precipitation for effecting the separation of rare earths. Welsbach used the double nitrates with ammonium nitrate in separating praseo- and neo-dymium. Urbani and Lacombe use the double rare earth magnesium nitrates, and since Bi Mg nitrate is isomorphous with these, it is used as an aid to crystallisation. Samarium is found in the earlier fractions and gadolinium in the last, and can be separated by this process, as can also gadolinium and europium.

The double Mg nitrates may be expected to fractionate in the following order : La, Ce, Pr, Nd, Sa, Gd, Y, Er, although each early

. fraction will contain two or three metals, but by repetition of the crystallisation separation may be effected.

Double sulphates with either K or Na are of great service, Ce, La, and didymium forming double salts insoluble in K_2SO_4 or Na_2SO_4, erbium, ytterbium, and yttrium yielding soluble sulphates.

Normal Na_2SO_3 gives quantitative precipitation with trivalent cerite earths. Th and Zr in excess of the precipitant give basic sulphites, soluble in excess.

Urbani also recommends crystallisation of the double ethyl sulphates, formed by adding barium ethyl sulphate to the earthy sulphate. The yttrium earths may be expected to crystallise in the following order: Yttrium, terbium, holmium, erbium, ytterbium.

Fractional or complete precipitation of certain metals with different reagents—many of them organic, such as metanitrobenzoic acid for thorium, or the great variation in solubility of the salts of m-nitrobenzene sulphonic acid ; the selective decomposition of the nitrates on heating, followed by extraction of the portion undecomposed, besides many other processes, have been more or less successfully employed.

TITANIUM, Ti'' and ^{iv}. Atomic weight, 48·1.—This, as well as the two next following metals (usually treated of in Group III., because they are precipitated by the group reagents chloride, sulphide, and hydroxide of ammonia), differ entirely from the previously treated metals. Their anhydrides, $Ti^{iv}O_2$, $Ta^{v}_2O_5$, and $Cb^{v}_2O_5$, are analogous to SiO_2, Sb_2O_5, &c., and are found in nature either in the uncombined state (TiO_2), or combined with various metallic bases, as titanates, tantalates, and columbates (niobates). The metal titanium has a great affinity for N, with which it combines directly.

Titanium is found as anhydride (almost pure) in the minerals rutile, anatase, and brookite ; combined with bases, chiefly lime, in titanite, $CaTiSiO_5$, in titaniferous iron, and in small quantities in many iron ores, in fire-clays, and generally in silicates (hence its occurrence in blast-furnace slags, as cyano-nitride, $TiCy_2,3Ti_3N_2$, in bright copper-coloured cubes).

Titanium forms several oxides, of which two are known with certainty, and one whose existence is probable, viz. :

TiO	Ti_2O_3	TiO_2.
Titanous oxide (probable).	Titanic oxide (sesquioxide).	Titanic anhydride.

The last oxide, acting as a weak base, and forming mostly very unstable salts, and likewise as an acid, is the only one which is of sufficient importance to be studied analytically.

In order to prepare some pure titanic anhydride, finely powdered rutile is fused with 3 parts of K_2CO_3, the fused mass powdered and treated with cold water, which removes SiO_2 and alkali silicates, and leaves insoluble potassium titanate, K_2TiO_3, together with ferric oxide. This is washed by decantation or on a filter, with cold water, and dissolved in cold dilute HCl. On diluting considerably with

water and heating to boiling, for some time, the whole of the titanium is precipitated as metatitanic hydroxide, H_2TiO_3 (Fe being held in solution by the acid), which differs from (ortho-) titanic acid in being quite insoluble in all acids, except strong sulphuric acid, whilst titanic hydroxide (obtained by precipitation with alkalies), of exactly the same composition, is readily soluble even in dilute H_2SO_4 or HCl. The precipitated metatitanic acid is usually tinged yellow, owing to some ferric oxide which is carried down with it. It is best, therefore, to filter off, to wash with a solution of ammonium chloride, and redissolve the precipitate in strong H_2SO_4. After dilution with water, it is reprecipitated once more by long-continued boiling, and is then all but free from iron. (Method of separation from Al, Gl, Y, and Th.) A more expeditious method for separating the iron oxide consists in precipitating the two metals from the dilute acid solution by means of ammonium sulphide, as FeS and H_2TiO_3, and to treat the precipitate with aqueous sulphurous acid, which dissolves the FeS and leaves the pure orthotitanic acid.

Another method consists in fusing the titanium compound with six times its weight of $KHSO_4$, till it yields a clear mass; dissolve in a large quantity of cold water, acidulate with dilute H_2SO_4, when metatitanic acid is precipitated as above. SiO_2, if present, is not attacked by $KHSO_4$, and remains in the insoluble residue.

Pure TiO_2 may also be obtained by fusion with acid potassium fluoride, and dissolving the fused mass in dilute HCl. Potassium titanic fluoride, K_2TiF_6, which is difficultly soluble in water (1 part requires 96 parts at $14°$ C.), is collected on a filter and washed with cold water, and purified by recrystallisation from boiling water. Its aqueous solution, when precipitated with ammonium hydroxide, yields titanic hydroxide, which on ignition is converted with incandescence into pure titanic anhydride—white when only feebly ignited, yellowish or brownish when intensely ignited.

SiO_2, or silicates, containing traces of TiO_2, may be decomposed with HF. H_2SO_4 must likewise be added in order to prevent a portion of the titanium from being volatilised with the SiF_4.

Metallic titanium may be obtained by reduction of the oxide in the electric furnace or by the aluminium powder reaction. Titanium forms alloys with iron, copper, and other metals. The alloys are in some cases very hard, ductile, and of considerable tensile strength.

Dry Reactions.

Titanium compounds, when heated on charcoal before the blowpipe, are not reduced to the metallic state (distinction from In). Heated in a borax bead (on charcoal), or, better still, in a bead of microcosmic salt, pure TiO_2, or a titanite, containing bases which do not themselves colour the borax bead, yields in the outer flame a colourless glass, but in the inner flame a glass which is yellow while hot, but assumes a violet colour on cooling. The reduction is

promoted by the addition of a little zinc or tin. If some $FeSO_4$ be added, the bead obtained in the inner flame becomes blood-red.

Reactions in Solution.

Use a solution of titanic acid in HCl.

Alkali hydroxides, sulphides, and carbonates, as well as $BaCO_3$, produce a bulky white precipitate of (ortho-) titanic hydroxide, H_2TiO_3, which is insoluble in an excess of the precipitants. When thrown down in cold solution, and washed with cold water, it is readily soluble in dilute HCl, or in dilute H_2SO_4. Washing with hot water converts it into insoluble metatitanic hydroxide. The presence of tartaric acid prevents the precipitation. (Iron, as well as Ni, Co, Zn, and U, which are precipitated by ammonium sulphide in the presence of tartaric acid and NH_4HO (the metal Mn is not), may thus be separated from TiO_2.)

K_4FeCy_6 produces a dark-brown precipitate.

Infusion of galls, brownish precipitate, which speedily turns orange-red.

HNa_2PO_4 throws down the titanic acid almost completely from an acid solution as a white gelatinous phosphate, which when washed and dried leaves a basic salt, probably $HTiPO_5, H_2O$.

Metallic tin or zinc, immersed in a HCl solution of TiO_2, evolves hydrogen, and reduces the TiO_2 to Ti_2O_3, which gives rise to a pale violet or blue coloration, and finally throws down a dark violet precipitate, which is rapidly oxidised to white TiO_2, with decomposition of the water, or when exposed to the air. This reaction frequently reveals the presence of TiO_2 in the analysis of iron ores during the process of reduction with zinc previous to the estimation of the iron by potassium permanganate.

TANTALUM, Ta^v. Atomic weight, 181.—This metal and columbium—or niobium, as it is sometimes called—occur only in a few minerals, found in a few localities, and then only in small quantities. The difficulty of detecting mere traces of them may account for their having been overlooked in others in which they have since been found—viz., in tinstone and wolfram.

In some of the minerals either tantalum or columbium (niobium) prevails, such as in tantalite and in columbite (niobite).

Tantalum and columbium (niobium) exist chiefly in the pentad condition, as is evidenced by the composition of their oxides (anhydrides), chlorides (which are volatile and decompose water), fluorides, &c. &c., viz. :

Tantalic anhydride, Ta_2O_5.	Chloride, $TaCl_5$.	Fluoride, TaF_5.
Columbic ,, Cb_2O_5.	,, $CbCl_5$.	,, CbF_5.

A lower oxide, $Ta^{iv}_2O_4$, and sulphide, $Ta^{iv}_2S_4$, are said to exist. In tantalates and columbates the acids closely resemble arsenic or phos-

phoric acid; they can exist as meta- $HTa(Cb)O_3$, pyro- $H_4Ta(Cb)O_7$, or ortho- $H_3Ta(Cb)O_4$, tantalic (columbic) acids.

Tantalic and *columbic anhydrides* are prepared from tantalites or niobites by fusing the finely powdered mineral with three parts of $HKSO_4$. The fused mass is extracted with water, whereby the bases are principally removed as sulphates. The residuary Ta_2O_5 and Cb_2O_5 are washed and fused once more with hydrogen potassium sulphate, &c. The residue, after having been well washed, is dissolved in HF, and a boiling solution of HF,KF gradually added to it. The liquid, on cooling or on concentration, yields a difficultly soluble potassium fluo-tantalate, $2KF,TaF_5$ (soluble in about 150–200 parts of water only), whilst the mother-liquors contain potassium fluo-oxy-columbate, $2KF,CbOF_3,OH_2$, which is soluble in 12·4 to 13 parts of water (distinction also from titanium, which forms $2KF,TiF_6$, soluble in 96 parts of water). These two salts may be purified by recrystallisation; and on decomposing them by heating with H_2SO_4 tantalic and columbic sulphates and potassium sulphate are left; this latter can be boiled out with water. When H_2SO_4 is expelled from the insoluble tantalic or columbic sulphate by strong ignition, or by heating in an atmosphere of ammonium carbonate, Ta_2O_5 or Cb_2O_5 is left.

TANTALUM.—Filaments of this element have recently been introduced as a substitute for carbon in electric lamps. Heated to a high temperature, it does not combine with oxygen if the pressure is less than 20 mm. Advantage is taken of this in its preparation, rods of the oxide being electrically heated *in vacuo*, when oxygen is evolved, a rod of the metal remaining.

Tantalum is remarkably hard, yet at the same time ductile, and its melting-point is very high—somewhere about 2250°. The red-hot metal decomposes water.

The anhydride, Ta_2O_5, is a white powder. When strongly ignited it turns a pale yellow, without emitting any light, and becomes insoluble in HCl or strong H_2SO_4 (distinction from TiO_2).

Fused with KHO, it is rendered soluble in water; fused with NaHO, it forms chiefly sodium metatantalate, $NaTaO_3$, insoluble in excess of NaHO, but soluble in water. When a solution of sodium hydroxide is added to this solution sodium tantalate is precipitated. Hydrated tantalic acid dissolves in HF, from a concentrated solution of which KF precipitates fine needle-shaped crystals of potassium fluo-tantalate. By prolonged boiling with water this soluble salt changes to an insoluble compound, $Ta_2O_5(2KF,TaF_5)$, the formation of which affords the means of detecting the smallest quantity of fluo-tantalate in mother-liquors containing potassium fluo-oxy-columbate (niobate).

Dry Reactions.

Microcosmic salt dissolves Ta_2O_5 to a colourless bead in both flames, and does not acquire a blood-red tint by the addition of ferrous sulphate (distinction from TiO_2).

Reactions in Solution.

Use a solution of $KTaO_3$ in water.

The tantalates of the alkali metals are soluble in water; all others (formed by double decomposition) are insoluble in water and decomposed by acids.

HCl precipitates Ta_2O_5 at first, then in excess redissolves it.

CO_2 passed through a solution of an alkali tantalate precipitates acid, or anhydro-tantalate.

NH_4HO precipitates from a HCl solution tantalic hydroxide, or an acid ammonium tantalate; tartaric acid prevents the precipitation.

Ammonium chloride or sulphate precipitates tantalic hydroxide, $HTaO_3$.

K_4FeCy_6 gives from acidified solutions a yellowish white precipitate, which turns brown by the addition of a few drops of ammonium hydroxide, and is soluble in larger quantities.

$K_6Fe_2Cy_{12}$, a yellow precipitate.

Infusion of galls, added to an acidified (H_2SO_4 or HCl) solution of an alkali tantalate, forms a light yellow precipitate, soluble in alkalies.

Metallic zinc and HCl do not reduce Ta_2O_5, and no blue coloration (or only a very faint one) is observed (distinction from Cb_2O_5).

COLUMBIUM, Cb (niobium, Nb). Atomic weight, 94. Specific gravity, 7·06. Melting-point, 1950°.—The metal has been obtained by electrolysis of its chloride and by reduction of the oxide by the aluminium reaction. It is extremely hard, scratching glass. It ignites when heated in oxygen to 400°, burning to form the pentoxide. It becomes incandescent when heated to 205° in chlorine. It combines energetically with some metals, e.g., platinum, at a high temperature.

Columbic anhydride, Cb_2O_5, is white, but turns transiently yellow when ignited. By strong ignition in hydrogen it is converted into Cb_2O_4. Like tantalic anhydride, it combines both with bases and acids. Concentrated sulphuric acid dissolves columbic anhydride, unless it has been too strongly ignited, and the solution remains clear on the addition of much water (distinction from Ta_2O_5).

Besides yielding salts of the ordinary type, the oxide, fused with alkalies, in presence of sodium fluoride to act as a flux, yields *columbates* (niobates), such as $Na_2O.Cb_2O_5$, $2Na_2O.Cb_2O_5$, and $2CaO.Cb_2O_5$.

Dry Reactions.

Microcosmic salt dissolves Cb_2O_5 readily. In the outer flame a bead, colourless whilst hot, is obtained; in the inner flame the bead acquires a violet, blue, or brown colour, according to the quantity of the acid present, and a red colour when a little ferrous sulphate is dissolved in it.

Reactions in Solution.

Use an aqueous solution of potassium columbate.

The columbates of the alkalies are nearly insoluble in water; all others are insoluble, but are decomposed by acids.

Mineral acids, especially sulphuric acid, even at the ordinary temperature, precipitate columbic hydroxide, nearly insoluble in the acid. (The precipitation of tantalic hydroxide requires the aid of heat.)

Oxalic acid does not affect the alkali columbates.

$(NH_4)_2S$ or NH_4OH precipitates from acidified solutions of Cb_2O_5 the hydroxide, containing ammonia, soluble in hydrofluoric acid.

NH_4Cl precipitates the acid, but only slowly and incompletely, more especially if in the presence of alkali carbonates.

K_4FeCy_6 gives, with a solution of an alkali columbate which has been acidulated with sulphuric or hydrochloric acid, a red precipitate.

$K_6Fe_2Cy_{12}$, a bright yellow precipitate.

Infusion of galls, an orange-red precipitate.

A piece of zinc immersed in an acidulated solution forms a beautiful blue precipitate, which after a time changes to brown. (Tantalates yield none, or only a faint blue colour.)

Cb forms also $CbCl_3$, $CbOCl_3$; the former decomposes CO_2 to CO.

KCNS in excess, and then pieces of Zn and strong HCl, gives a bright golden red colour, affording a delicate test for columbium.

Rare Metals precipitated by the Group Reagents NH_4Cl, NH_4OH, and $(NH_4)_2S$ in the Form of Sulphides.

URANIUM, U", [iv], and [vi], and pseudo-triad. Atomic weight, 238·5. —Uranium is not a very abundant metal; it is found principally in pitch-blende, which contains from 40 to 90 per cent. of uranoso-uranic oxide, U_3O_8; in uranium ochre, or sulphate; and in uranite or uranium mica, which is a calcium (cupric) uranic phosphate. In small quantities it exists in several rare minerals, such as euxenite, yttrotantalite, &c.

This element has specific gravity = 18·7, is a little harder than iron, and about the colour of nickel.

It is very difficult to reduce by C or H from its oxide, but may be obtained by electrolysis of the chloride, or from the oxide with carbon in the electric furnace.

The finely divided metal ignites in oxygen at 170°, and also combines directly with nitrogen.

Uranium salts are almost always obtained from pitch-blende. The U_3O_8 therein is associated with sulphur, arsenic, lead, iron, and several other metals. The mineral is finely powdered, freed by elutriation or washing from the lighter earthy impurities, roasted for a short time to remove part of the sulphur and arsenic, then dissolved in nitric acid, and the solution evaporated to dryness. The residue is exhausted with water, and the solution filtered from a brick-red residue of ferric oxide, ferric arsenate, and lead sulphate. On evaporation the aqueous solution yields crystals of the nitrate, which by dissolving in ether and setting aside for

spontaneous evaporation are obtained pure. When recrystallised once more from boiling water they consist of pure uranylic nitrate, $UO_2(NO_3)_2,6OH_2$, in which $(UO_2)''$, uranyl, acts as a dyad radical.

Various uranium minerals have been found to contain " radium," " emanium," &c., or radio-active matter. The extraction and concentration of these substances is an extremely tedious process, and quite beyond the scope of this book.

Uranium exists as a dyad and pseudo-triad element. It forms with oxygen two salt-forming oxides and several compound oxides:

Uranous oxide.	Trioxide.	Compound oxides.		Uranous chloride.
UO_2	UO_3	U_3O_8 or $UO_2 + 2UO_3$ (dark green)	UO_5 or $UO_3 + UO_2$ (black)	UCl_4
	Uranylic chloride. $(UO_2)Cl_2$	Pentachloride. UCl_5	Uranous sulphate. $U(SO_4)_2$	Uranylic sulphate. UO_2SO_4.

Uranic oxide in a hydrated state combines both with acids to form uranylic salts, and with the oxides of the more electro-positive metals to form acid uranates, of the general formula $R'_2(UO_2)_2O_3$, analogous to dichromates, disulphates, &c. These are yellow, insoluble in water, but are decomposed by acids. Disodium diuranate (uranium yellow) is used as a pigment in glass and porcelain manufactures.

Dry Reactions.

Borax and microcosmic salt give with uranium compounds in the inner flame of the blowpipe green beads, in the outer flame yellow beads, which acquire a yellowish green tint on cooling. The oxides of uranium are not reduced by fusion with Na_2CO_3 on charcoal.

Reactions in Solution.

(A) **URANOUS COMPOUNDS.**—Use a solution of uranous sulphate, $U(SO_4)_2$; prepared by dissolving uranoso-uranic oxide in hot oil of vitriol, diluting with water and evaporating *in vacuo*.

Uranous salts constitute powerful reducing agents. They are green, or greenish white, and yield green aqueous solutions.

$(NH_4)_2S$ forms a black precipitate of uranous sulphide, US.
Alkalies throw down red-brown gelatinous uranous hydroxide, $U(HO)_4$.
Alkali carbonates precipitate green uranous hydroxide, soluble in excess, especially in excess of ammonium carbonate.

Uranous salts become oxidised to uranic salts by exposure to air, or by treatment with nitric acid, &c. Gold and silver salts are speedily reduced by them, and ferric salts are reduced to ferrous salts.

(B) **URANIC COMPOUNDS.**—Use a solution of uranylic nitrate, $UO_2(NO_3)_2$.

Uranic salts are yellow, they are mostly soluble in water, and are reduced to uranous salts by SH_2 and by alcohol, or ether and in sunlight.

$(NH_4)_2S$ produces in cold solutions a chocolate-brown precipitate of uranylic sulphide, containing also ammonium sulphide and water. It is insoluble in yellow ammonium sulphide. On warming or boiling the liquid which contains the uranylic sulphide, $(UO_2)S$, suspended in it, the precipitate splits up into sulphur and the black oxide, UO, which is insoluble in excess of the sulphide. Uranylic sulphide dissolves readily in neutral ammonium carbonate. (Method of separation of U from Zn, Mn, and Fe.)

Alkali hydroxides produce a yellow precipitate, consisting of acid uranate of the alkali metal; insoluble in excess of the precipitant; not precipitated in the presence of tartaric acid.

The ammonium precipitate is soluble in a solution of ammonium carbonate, and ammonium sulphide does not precipitate the uranium from this solution.

Alkali carbonates give a light yellow precipitate, consisting (in the case of potassium carbonate) of potassio-uranic carbonate; readily soluble in an excess of the precipitant. By treating the liquid with dilute sulphuric acid, as long as effervescence takes place, an acid uranate is precipitated. (Method of separation of U from Al and Fe^{iv}.)

$BaCO_3$ completely precipitates a solution of a uranic salt, even in cold solutions. (Separation of U from Ni'', Co'', Mn'', Fe'', and Zn.)

K_4FeCy_6 produces a reddish brown precipitate. (Most delicate special reaction.)

$K_6Fe_2Cy_{12}$ produces no change.

Metallic zinc does not precipitate metallic uranium from its solutions.

THALLIUM, Tl' and $'''$. Atomic weight, 204·1.—This metal was discovered by Crookes in 1861. It occurs in many kinds of copper and iron pyrites, but invariably in very minute quantities; also in many kinds of crude sulphur, in some of the deposits from the flues leading from the pyrites furnaces to the lead chambers of sulphuric acid works, and in the deposits in the chambers themselves. It has, moreover, been found in lepidolite, in preparations of cadmium and bismuth, in ores of zinc, mercury, and antimony, in the ashes of some plants, and in some saline waters, &c. &c.

The metal is most economically extracted from thalliferous flue-dust. The dust is stirred up with boiling water, the insoluble portion allowed to settle, and the clear supernatant liquid syphoned off. On the addition of concentrated hydrochloric acid impure

thallious chloride, TlCl, is precipitated. This impure chloride is dissolved in concentrated sulphuric acid, evaporated till the hydrochloric acid, as well as the greater portion of the sulphuric acid, has been driven off, then dissolved in boiling water, and a rapid current of sulphuretted hydrogen passed through the solution, whereby all the metals of the SH_2 group are precipitated. On now introducing plates of zinc into the dilute acid filtrate, spongy metallic thallium is precipitated, which can be readily removed from the zinc, and obtained in lumps or bars by pressure. It must be preserved under water.

It is softer than lead, and of the same colour, of specific gravity 11·8. It melts at 290° C., and may be distilled in hydrogen. The metal and all its salts are highly poisonous, and should not be touched with the fingers or be allowed to fly about as dust.

The salts may be prepared by dissolving the metal in the respective acids, or by the double decomposition of soluble thallium salts.

Thallium forms two series of compounds—thallious and thallic. In the thallious the metal exists as a monad, and in the thallic as a triad. Thus we have :

Thallious oxide	. Tl_2O	Thallic oxide	. Tl'''_2O_3
Thallious chloride	. TlCl	Thallic chloride	. $Tl'''Cl_3$, &c.,
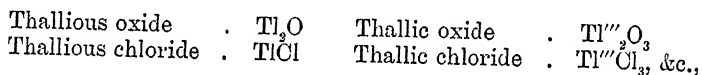
together with several intermediate compounds.

In some of its chemical relations thallium differs from all other metals. It many respects it resembles the alkali metals, as, for instance, in forming the readily soluble and highly alkaline thallious oxide and carbonate ; an insoluble double platinum salt, Tl_2PtCl_6 ; an alum analogous to ordinary potash alum, $Tl_2SO_4.Al_2(SO_4)_3 24H_2O$; and a series of thallious phosphates analogous to the alkaline phosphates. In most other respects, however, it is more nearly allied to the heavy metals, especially to lead, which it resembles closely in appearance, density, melting-point, specific heat, and electric conductivity, also in forming insoluble chlorides and iodides.

Thallium compounds impart an intense green colour to the blowpipe flame. The spectrum of thallium shows one very striking emerald-green line, Tlaλ, and hence its name, from θαλλός, a green budding twig.

Reactions in Solution.

(A) **THALLIOUS COMPOUNDS.**—Employ a solution of thallious sulphate, Tl_2SO_4, or nitrate, $TlNO_3$.

Thallious salts are for the most part colourless and soluble in water, such as the nitrate, sulphate, phosphate, tartrate, and acetate. Some are difficultly soluble, e.g., the carbonate and chloride, and a few are almost insoluble, e.g., the iodide. They react neutral to test-paper, and possess a slight metallic taste. Thallious oxide, Tl_2O, is colourless and fusible ; it dissolves in water—the solution is

colourless, alkaline, caustic, and absorbs carbon dioxide from the air. It also dissolves in alcohol.

Thallious salts are with difficulty converted into thallic salts; powerful oxidising agents, such as nitric acid, are without effect on them. They require boiling and evaporating with aqua regia to convert them into the so-called higher stage of activity.

SH_2 does not precipitate strongly acidified thallious solutions unless As_2O_3 be present, when a part of the thallium is carried down with the arsenious sulphide, as a brownish red precipitate. Neutral or very slightly acidified solutions are incompletely precipitated by SH_2. From acetic acid solutions the whole of the thallium is thrown down as black thallious sulphide, Tl_2S.

$(NH_4)_2S$ (group reagent) precipitates the whole of the thallium as thallious sulphide, insoluble in ammonium hydroxide, alkali sulphides, or potassium cyanide. Readily soluble in dilute hydrochloric, sulphuric, or nitric acids, but only slightly soluble in acetic acid. When exposed to air thallious sulphide is rapidly converted into thallious sulphate. On heating it fuses and volatilises.

Alkali hydroxides do not precipitate aqueous solutions of thallious salts.

Carbonated alkalies produce a precipitate only from concentrated solutions, Tl_2CO_3 being soluble in 20 parts of water.

HCl or a soluble chloride throws down white thallious chloride, TlCl; the precipitate subsides readily, and is unalterable in the air. It is very slightly soluble in boiling water, and still less so in hydrochloric acid.

KI precipitates, even from the most dilute thallious solutions, light yellow thallious iodide, TlI, which is almost entirely insoluble in water, but somewhat more soluble in a solution of potassium iodide. This constitutes the most delicate reaction for thallious salts.

K_2CrO_4 precipitates yellow thallious chromate, Tl_2CrO_4, insoluble in cold nitric or sulphuric acid.

$PtCl_4$ precipitates difficultly soluble, pale orange-coloured thallious platinic chloride, $2TlCl,PtCl_4$.

Zinc precipitates metallic thallium.

(B) THALLIC COMPOUNDS.—Employ a solution of thallic chloride, $TlCl_3$.

Thallic salts are easily distinguished from thallious salts by their behaviour with caustic and carbonated alkalies, which precipitate brown gelatinous thallic hydroxide, TlOHO, insoluble in excess.

Thallic oxide is scarcely acted on by cold concentrated sulphuric acid; on heating, thallic sulphate, $Tl_2(SO_4)_3,7OH_2$, is obtained. When a solution of thallic sulphate is boiled oxygen is given off, and a thallious salt left. When treated with HCl thallic oxide

yields the chloride $TlCl_3$ as a white crystalline mass, which on heating splits up into $TlCl$ and Cl_2.

> HCl or a soluble chloride produces no precipitate.
>
> SH_2 reduces thallic to thallious salts, with precipitation of sulphur.
>
> $H_2C_2O_4$ produces a white pulverulent precipitate of oxalate.
>
> HNa_2PO_4 gives a white gelatinous precipitate.
>
> H_3AsO_4 or a soluble arsenate gives a yellow gelatinous precipitate.
>
> K_2CrO_4 does not precipitate thallic salts.
>
> KI gives a precipitate of TlI and I_2.

INDIUM, In^{iv}, and pseudo-triad. Atomic weight, 115. Specific gravity, 7·42. Melting-point, 176°.—Has hitherto only been found as a rare and insignificant constituent of some zinc ores (zinc-blende from Freiberg), in the metallic zinc prepared from these ores, and in tungsten.

Indium is a white, highly lustrous metal resembling platinum, soft and ductile. It is not oxidised in the air or in water, but heated to a high temperature burns with a blue flame, forming In_2O_3. Dilute HCl or H_2SO_4 dissolves it readily, hydrogen being given off. Concentrated sulphuric acid dissolves it with evolution of SO_2. It is readily soluble also in cold dilute nitric acid. The oxide, In'''_2O_3, is brown when hot, straw-coloured when cold, and is readily reduced when heated on charcoal, or in a current of hydrogen gas. A black dioxide, $In^{iv}O_2$, exists likewise.

The principal salts of indium, viz., the sulphate, $In_2(SO_4)_3,9OH_2$, the nitrate, $In(NO_3)_3$, and the chloride, $InCl_3$, are freely soluble in water. The chloride is volatile and hygroscopic.

Dry Reactions.

Indium and its compounds impart to the flame a peculiar bluish tinge. When examined with the aid of a spectroscope two characteristic blue lines can be seen, a bright one in the blue λ, and a feebler one in the violet λ. They are, however, very transient. The sulphide gives more persistent lines than the chloride.

Reactions in Solution.

A solution of any of the above salts may be used.

> SH_2 produces no precipitate in the presence of a strong acid. Indium is, however, precipitated like the metal zinc from slightly acid solutions, or in the presence of acetic acid. The slimy precipitate of indium sulphide, In_2S_3, is of a fine yellow colour.
>
> $(NH_4)_2S$ produces at first from a solution containing ammonium tartrate a white precipitate, said to consist of In_2S_3 and hydrogen. It turns yellow on the addition of acetic acid. The sulphide is insoluble in cold, but soluble in the hot sulphide, and on cooling it separates again of a white colour.

Alkali hydroxides produce a white bulky precipitate of indium hydroxide, $In(HO)_3$, resembling aluminium hydroxide, quite insoluble in alkalies. The presence of tartaric acid prevents the precipitation.

Alkali carbonates precipitate white gelatinous carbonate. When recently precipitated it is soluble in ammonium carbonate, but not in the fixed alkali carbonates. On boiling indium carbonate separates again.

$BaCO_3$ precipitates indium salts in the cold as basic salts. (Distion from Zn, Mn, Co, Ni, and Fe.)

HNa_2PO_4 throws down a bulky white precipitate.

Alkali oxalates produce a crystalline precipitate.

Zinc precipitates the metal in the form of white shining laminæ.

VANADIUM, V''' and ^{v}. Atomic weight, 51·2; specific gravity = 5·5.—It oxidises in the air, but resists most acids and alkalies. Occurs only in a few rare minerals, principally in vanadite, or lead vanadate and oxychloride, $Pb_2V_3ClO_{12}$, analogous in composition to pyromorphite, also to a very small extent in many iron ores (clay and pea iron ores), and, as Roscoe discovered, in the copper-bearing beds at Alderley Edge, and Mottram St. Andrew's, Cheshire.

Vanadium has recently been introduced into certain special steels, to which it is said to impart great resistance to shock. The metal can be obtained in a compact state by the reduction of V_2O_5 by aluminium powder.

Vanadite, or mottramite, $(PbCu)_3(VO_4)_3$, may be made the starting-point for preparing the several vanadium compounds. The mineral is dissolved in nitric acid, and the lead and arsenic precipitated by SH_2, which at the same time reduces the vanadic pentoxide, V_2O_5, to tetroxide, V_2O_4. The blue filtered solution is then evaporated to dryness, and the residue digested in ammonium hydroxide, when the vanadic tetroxide becomes reoxidised into pentoxide. The ammonium vanadate can be precipitated as a white powder from this solution by introducing a lump of sal ammoniac, being scarcely soluble in a saturated solution of this salt. By exposure to a temperature below redness in an open crucible ammonia is expelled and V_2O_5 is left.

The mineral may also be fused with a mixture of $NaHO$ and KNO_3, when soluble vanadates are produced, and on saturating the clear solution with NH_4Cl ammonium metavanadate separates out.

Vanadium forms several oxides, oxychlorides, chlorides, sulphides, which show that the metal is closely allied to the phosphorus and arsenic group. Thus:

Oxides.	Oxychlorides.	Chlorides.	Sulphides.
V_2O	—	—	—
V_2O_2	—	VCl_2	—
V_2O_3 (black)	—	VCl_3	—
V_2O_4 (blue)	—	VCl_4	V_2S_4
V_2O_5	$VOCl_3$	—	V_2S_5

25

The most important of these compounds is the pentoxide, or vanadic anhydride, analogous in composition with phosphoric, arsenic, antimonic, tantalic, and columbic anhydrides. It combines in different proportions with bases, forming, like the other anhydrides referred to, three series of salts, viz., ortho-, pyro-, and meta-vanadates. Fused with Na_2CO_3, it yields sodium orthovanadate, Na_3VO_4; but, when boiled with a solution of an alkali it forms the metavanadate, the latter class of vanadates being more stable than the ortho salts. Alkali vanadates are soluble in water inversely to the quantity of free alkali or alkaline salt present. Hence they are precipitated from their solutions by excess of alkali, or by salts as NH_4Cl. (Most characteristic reaction.)

Vanadic anhydride has a reddish yellow colour, and is difficultly soluble in water (1000 parts), forming a light yellow solution which reddens litmus paper. It dissolves also in the stronger acids to red or yellow solutions, which become frequently decolorised by mere boiling. It unites, however, with bases more readily than with acids.

A sulphuric acid solution of the acid, when considerably diluted with water, and treated with zinc or sodium amalgam and warmed gently, turns first blue, then green, and finally from lavender to violet. The V_2O_5 becomes reduced to V_2O_2; and on the addition of NH_4HO a brown precipitate of the hydroxide of the dioxide (hypo-vanadious acid) forms, which absorbs oxygen more rapidly than any other known reducing agent, and bleaches organic colouring-matter (indigo solution, &c.) as quickly as chlorine.

Many organic substances, such as oxalic or tartaric acid, sugar, alcohol, reduce vanadic acid, especially in the presence of strong mineral acids, to the blue V_2O_4. The same takes place when SO_2 or SH_2 is added to its solutions in acid.

Dry Reactions.

Borax dissolves V_2O_5 to a clear bead, colourless, or, with large quantities of the anhydride, yellow, in the outer flame, beautiful green in the inner flame. With larger quantities of vanadic acid it looks brownish whilst hot, and only turns green on cooling.

Reactions in Solution.

Use a solution of sodium metavanadate, $NaVO_3$.

Orthovanadates are generally yellow or reddish yellow, both in the liquid and solid state. By boiling in water the orthovanadates of the alkalies are converted into colourless metavanadates. On the addition of an acid to a solution of neutral or orthovanadate the solution becomes yellowish red, owing to the formation of anhydro salts.

Ammonium, barium, and lead metavanadates are but sparingly soluble in water. The alkali vanadates are more soluble in pure water than in water containing free alkali or a salt; hence they are precipitated in the presence of the latter. All are soluble in nitric acid, but insoluble in alcohol.

$(NH_4)_2S$ (group reagent) produces a brown coloration in the liquid, and on acidulating with HCl, or, better, with H_2SO_4, the

soluble ammonium sulphovanadate is decomposed, and brown pentasulphide, V_2S_5, mixed with sulphur, is precipitated ; the liquid at the same time generally acquires a blue colour.   It dissolves with red-brown colour in aqueous solutions of alkali carbonates, hydroxides, and sulph-hydrates.

If an acidified solution of an alkali vanadate be shaken up with ether containing peroxide of hydrogen, the aqueous fluid acquires a red-brown colour, like that of ferric acetate, whilst the ether remains colourless.   This reaction is extremely delicate.

Tincture of gall-nuts, made by boiling a few gall-nuts in water and filtering the solution, gives with traces of a vanadate, such as the ammonium or sodium salt, an intense violet-black coloration. This strongly coloured liquid can be used as an ink, but is speedily spoiled by steel pens.

Vanadic and chromic acids are the only acids whose salts give rise to red-coloured solutions.   They are, however, differently affected by reducing agents.

Many of the elements which are so difficult to reduce to a metallic state, such as uranium, vanadium, tungsten, titanium, and some of the cerium metals, reduce and melt in the electric furnace. They take up carbon, in varying amounts, however, and in some cases form definite carbides after the manner of calcium.

In some cases also these metals can be reduced by heating their oxides with finely powdered aluminium.

Reduction of Titanic, Vanadic, Tungstic, and Molybdic Acids by Nascent Hydrogen—Colours produced.

Zinc with HCl or H_2SO_4, acids so dilute that evolution of H just appreciable.

TiO_2—Very pale blue or lilac coloration.

Alkali titanates—Pale violet, rapidly becoming dark blue.

{ MoO_3—Brown, soon becoming green.
  Molybdates—Reddish brown coloration, then greyish brown precipitate.

{ WO_3
  Tungstates } Pale blue, gradually darkening.

Vanadic acid—Requires more acid to be present for reduction—green colours.
Vanadates (over 1 per cent.)—Violet, pale blue, greyish blue colours.

REACTIONS OF THE RARE METALS OF GROUP II.

Group II. comprises the rare metals precipitated as sulphides by SH_2 from a hydrochloric acid solution, viz. :

(A) *As sulphides, insoluble in yellow ammonium sulphide :* Palladium, rhodium, osmium, ruthenium.

These four metals are generally found ssaociated in platinum ores, together with iridium, and hence are frequently termed platinum metals. Platinum gives a sulphide insoluble in $(NH_4)_2S$, and its reactions are given in detail on p. 220. Iridium sulphides differ from the others in being soluble in $(NH_4)_2S$ (see p 395).

The atomic weights and specific gravities of the six platinum metals are :

	Ru.	Rh.	Pd.	Os.	Ir.	Pt.
Atomic weight	85·5	103·0	106·5	191	193	194·8
Specific gravity	12·26	12·1	11·9	22·4	22·4	21·5

It will be noted that three of these metals have only about half the density of the remaining three.

PALLADIUM, Pd″ and ^{iv}. Atomic weight, 106·5.—Occurs native in platinum ores, principally, however, alloyed with gold and silver, in a gold ore found in Brazil. The gold dust is fused together with silver, and the granular alloy heated with nitric acid, in which silver and palladium only dissolve. On the addition of sodium chloride, silver is removed as chloride, and the palladium may then be precipitated as palladious cyanide by means of mercuric cyanide, and the $PdCy_2$ decomposed by ignition.

The metal resembles platinum, but is somewhat darker in colour. Its specific gravity is 11·9. Of all the so-called platinum metals it fuses most readily (1587°). Palladium is sparingly soluble in pure nitric acid, but dissolves more readily in the red acid. It dissolves slightly in boiling concentrated sulphuric acid, and is readily attacked by fusing with hydrogen potassium sulphate. The best solvent for it, as for most other platinum metals, is aqua regia. The metal oxidises when heated in air, the surface becoming coloured from films of oxide. It absorbs hydrogen to a large extent, and if heated over a spirit lamp or gas flame will even decompose the hydrocarbon vapours, carbon being deposited on the metal. Palladium forms two distinct sets of oxides and chlorides, in which the metal exists either as a dyad or tetrad, thus :

| Palladious oxide . | . PdO | Chlorides | . $PdCl_2$ |
| Palladic   ,, | . PdO_2 | ,, | . $PdCl_4$ |

PALLADIOUS SALTS.

The oxide, PdO, is obtained on gently igniting palladious nitrate. It is black, and its hydroxide dark brown. Both part with their oxygen upon ignition, leaving spongy palladium. The nitrate may be prepared from the metal by dissolving in nitric acid and concentration over a water-bath. It forms then a brownish red non-crystallisable mass.

Palladious salts are mostly soluble in water; they are brown or reddish brown; their dilute solutions are yellow.

Reactions in Solution.

A solution of palladious nitrate, $Pd(NO_3)_2$, is most easily obtained for these reactions.

- H_2O precipitates a brown basic salt from solutions containing slight excess of acid only.

  SH_2, or $(NH_4)_2S$, throws down from acid or neutral solutions black palladious sulphide, PdS, insoluble in alkali sulphide, but soluble in boiling hydrochloric acid, and readily soluble in aqua regia.

  KHO, or NaHO, precipitates a yellowish brown basic salt, soluble in excess.

  Soluble carbonates precipitate brown palladious hydroxide, $Pd(HO)_2$, soluble in excess, reprecipitated on boiling.

  NH_4HO or carbonate produce no precipitate from the nitrate, but decolorise the dark brown solution, forming double palladammonium salts.* A somewhat transient blue colour is formed by ammonium hydroxide alone.

  HI or soluble iodides give, even in very dilute solutions, a black precipitate of palladious iodide, PdI_2, somewhat soluble in excess of KI. (Most characteristic reaction for Pd.) It serves for the detection of iodine in the presence of chlorine and bromine.

  $HgCy_2$ gives a yellowish white gelatinous precipitate of $PdCy_2$, readily soluble in KCy and in ammonium hydroxide. Slightly soluble in HCl. It leaves on ignition spongy metallic palladium. (Characteristic reaction.)

  NH_4Cl does not readily precipitate palladium salts.

  KCl precipitates a brownish red octahedral double chloride, $2KCl,PdCl_2$, insoluble in absolute alcohol; soluble in water to a dark red fluid.

  NH_4SCN gives no precipitate even after the addition of SO_2. (Distinction from Cu.)

  $SnCl_2$ produces a brownish black precipitate, soluble in HCl to an intense green solution.

An iodine solution stains palladium black, but has no effect on platinum.

Palladious salts are reduced to the metallic state by phosphorus,

---

* Palladium shows a very strong tendency to form compounds containing NH_2 or (NH_3) (?). A great number of these are known. It is a point of resemblance of this metal to copper and cobalt and nickel. Undoubtedly they are amines—that is, derivatives of ammonia in which one or more hydrogen atoms from one or more molecules of NH_3 have been replaced by the metal. Some of the hydrogen atoms in NH_3 seem to be decidedly labile. The solution in ammonium hydroxide (above) is faintly blue, like copper, but fades rapidly, a palladammonium hydroxide, $PdN_2H_6(OH)_2$, being formed. This forms a series of salts with acids, as $PdN_2H_6 2HCl =$

$$Pd \begin{cases} NH_2HCl \\ NH_2HCl \end{cases}$$
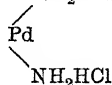
sulphurous, nitrous and formic acids, metallic zinc or iron, alcohol, and other organic compounds.

Palladious chloride, obtained by dissolving PdS in boiling HCl, is precipitated by NH_4HO as flesh-coloured palladammonium chloride, $Pd(NH_3)_2Cl_2$, soluble in excess to a colourless fluid, from which HCl reprecipitates it as a yellow crystalline chloride, identical in composition.

All palladium compounds are decomposed when ignited.

PALLADIC SALTS.

$PdCl_4$ is known only in solution. It is obtained when the metal is dissolved in aqua regia or when the oxide, PdO_2, is dissolved in strong HCl. $PdCl_4 2NH_4Cl$ is formed as a bright red almost insoluble crystalline powder when NH_4Cl is added to the $PdCl_4$ solution and boiled, or when a palladious salt, as PdN_2O_6, is boiled with HCl and NH_4Cl added.

KHO added to the $PdCl_4$ solution or the $PdCl_4 2KCl$ solution and boiled gives a black precipitate of PdO_2. In cold solutions a brown hydroxide is formed. They both dissolve very slowly in HCl, sometimes giving off free chlorine.

The double chloride above mentioned is probably
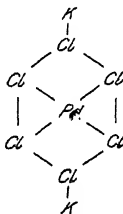
and a number of amines are no doubt similarly constituted.
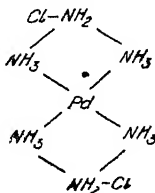
Palladic sulphide also forms double salts with alkali and other sulphides.

Hydrazine (N_2H_4) salts reduce Pd from acid solutions.

Potassium nitrite and excess of an alkali hydroxide, at a low temperature, form a crystalline precipitate of palladium potassium nitrite.

RHODIUM, Rh'', ^{iv}, and ^{vi}, also a pseudo-triad. Atomic weight, 103·0.—Found in small quantity in platinum ores, and frequently to

a considerable extent in platinum residues—that is, the insoluble portion after treating the platinum mineral with aqua regia, in which it is insoluble.

It is a whitish grey metal, less ductile than platinum, and scarcely softened even in the flame of the oxyhydrogen blowpipe. The specific gravity of unfused rhodium is 10·64, that of the pure metal, after fusion, 12·1. An alloy of this metal with platinum is employed in electric-resistance pyrometers for high, furnace, temperatures. Rhodium is unalterable in the air at ordinary temperatures, but oxidises at a red heat. It also combines with chlorine at a red heat. When pure and in a compact state it resists the action of the strongest acids, even of aqua regia; but when alloyed with other metals, as with Pb, Bi, Cu, and Pt, it is soluble in aqua regia; when, however, alloyed with Au or Ag it does not dissolve. It is oxidised by fusion with dry potassium hydroxide and nitre. Fusion with hydrogen potassium sulphate converts it into soluble potassium rhodic sulphate, $K_6Rh_2(SO_4)_6$. Mixed with sodium chloride and ignited in a current of chlorine, a double chloride of sodium and rhodium, $3NaCl,Rh'''Cl_3 + H_2O$, is formed, which is likewise easily soluble in water, forming a rosy red solution. Hydrogen is absorbed by rhodium powder even to a greater extent than by palladium. This form of the metal also decomposes the vapour of several carbon compounds, as ethylene, acetylene, &c.

Rhodium forms several oxides, chlorides, sulphides, &c., in which the metal exists as a dyad, tetrad (pseudo-triad), or hexad element, thus:

		Oxides.
Rhodious oxide	. . . . . .	RhO
Rhodic „	. . . . . .	Rh_2O_3
„ dioxide	. . . . . .	RhO_2
Rhodic trioxide (anhydride, acting as a weak acid) .		RhO_3
„ tetrahydroxide .	. . . . .	$Rh(OH)_4$

	Chlorides.		Sulphides.
Rhodious chloride	. $RhCl_2$.	Rhodious sulphide .	RhS
Rhodic chloride	. $RhCl_3$	Rhodic „ .	Rh_2S_3
	or Rh_2Cl_6		

Rhodium salts are obtained with difficulty, owing to the insolubility of the metal and its oxide in acids. Their solutions are rose-coloured.

Reactions in Solution.

Employ a solution of potassio-rhodic sulphate, or of the double chloride of sodium and rhodium.

Soluble sulphides precipitate from a hot solution brown rhodic sulphide, Rh_2S_3, insoluble in ammonium sulphide, but soluble in boiling nitric acid.

KHO, or NaHO, gives with the chloride a yellowish brown precipitate of rhodic hydroxide, $Rh_2(HO)_6$, soluble in excess; in other rhodic salts this precipitate appears only on boiling. If the gases produced by the action of HCl on $KClO_3$ be passed into the alkali solution of $Rh_2(OH)_3$, a blue colour is finally produced, owing to the formation of sodium perrhodate, Na_2RhO_4. SO_2 reduces and decolorises this compound.

From a solution of rhodic chloride, KHO, producing at first no precipitate, gives on the addition of alcohol a brown precipitate of rhodic hydroxide.

NH_4OH gives also a yellow flocculent precipitate, only formed, however, after some time, soluble in HCl, forming a rhodamine salt.

KI produces a slight yellow precipitate.

Metallic zinc precipitates black metallic rhodium.

KNO_2 (potassium nitrite) gives with the chloride an orange-yellow precipitate, which is slightly soluble in water, and only very slowly decomposed by strong HCl; characteristic.

Rhodium is distinguished from the other platinum metals by its insolubility in aqua regia, its solubility in fusing $KHSO_4$, and the behaviour of its chloride with KHO and alcohol.

Rhodium exhibits even a greater power than palladium to form amines or rhodium bases. A great number of these have been made, but there is still no certainty as to their constitution. Some are colourless, others rosy-red, and others, again, of a more or less marked purple colour.

The following are cited as types only of some of these :

Roseo-rhodium chloride $= Rh_2 10NH_3Cl_6(H_2O)_2$.
Luteo   ,,   ,, $Rh_2 12NH_3Cl_6$.
Purpureo ,,   ,, $Cl_2(Rh_2 10NH_3)Cl_4$.
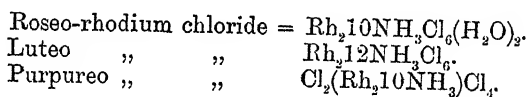
The constitution of the last class may possibly be expressed by :
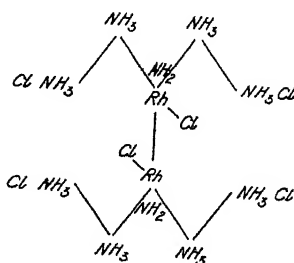
OSMIUM, Os'', ^{iv}, ^{vi}, and ^{viii}, also a pseudo-triad. Atomic weight, 191.—Found chiefly as a natural alloy of osmium iridium in platinum ores, which remains behind undissolved, when the ores are

treated with aqua regia, in the form of white, metallic-looking, hard grains. This alloy is attacked by mixing it with common salt, or potassium chloride, and exposing it in a glass or porcelain tube to a current of moist chlorine gas. Osmic acid is formed, which volatilises below 212° C., and can be condensed and fixed by passing the fumes into a solution of an alkali. (Iridium remains behind in the tube as a double chloride, $2KCl,IrCl_4$. This salt is obtained in reddish black regular octahedra by recrystallisation from water.) The alkali solution is evaporated with excess of sal ammoniac, and leaves on ignition of the dry residue, and extraction with water, metallic osmium, as a black or grey powder, and with metallic lustre. The densest metal has a specific gravity of 21·4. Intense white heat volatilises the metal, but does not melt it, the melting-point being about 2500°. The metal is employed in the filament form in electric glow lamps in the same manner as carbon. In contact with air it burns the more readily the finer the metal is divided, and is converted into osmic anhydride, $Os^{viii}O_4$. Red fuming nitric acid, or aqua regia, dissolves osmium likewise, and oxidises it to OsO_4. Very intensely ignited, osmium is rendered insoluble in acids, and has to be fused with nitre and then distilled with nitric acid, when OsO_4 distils over.

Osmium combines with oxygen, or chlorine, &c., in several proportions, thus:

Osmious oxide	.	OsO	Osmious chloride .	.	$OsCl_2$
Osmic „	.	Os_2O_3	——		—
Osmium dioxide	.	OsO_2	Osmic tetrachloride	.	$OsCl_4$
Osmium tetroxide .		OsO_4	——		—

The two highest oxides combine with bases, and form osmites and unstable osmates. OsO_4 is remarkable for its peculiar, exceedingly irritating, and offensive odour, resembling that of Cl and I. It attacks the eyes and the air passages, and is excessively poisonous. It is soluble in water, the solution being neutral, and is precipitated from its solutions by all metals, even by mercury and silver, as a black metallic powder. On heating a mixture of finely divided osmium, or of the sulphide, with potassium chloride in a stream of chlorine gas, a double chloride, $Os_2Cl_6 6KCl,3OH_2$, is obtained, which crystallises from water in dark red-brown regular octahedra. The salt is insoluble in alcohol.

The solution of this double chloride is more stable than that of the osmium chlorides, and may conveniently be employed for studying the reactions.

All compounds of osmium yield the metal when ignited in a current of hydrogen.

Reactions in Solution.

SH_2 or sulphides give a brownish black sulphide, OsS, which only separates when a strong acid is present. The precipitate is insoluble in ammonium sulphide.

Alkalies, or their carbonates, produce a brownish red precipitate of hydrated osmic dioxide, $Os(HO)_4$.

On fusing the double chloride with Na_2CO_3, dark grey OsO_2 is obtained.

Heated with tannic acid, or alcohol, with addition of HCl, the double chloride is reduced to the blue osmious chloride, $OsCl_2$.

A solution which contains osmic acid (and osmate) is remarkable for its great oxidising power. It decolorises indigo solution, separates iodine from KI, converts alcohol into aldehyde and acetic acid. Sodium sulphite yields a deep violet coloration, and dark blue osmious sulphite, $OsSO_3$, gradually separates. Ferrous sulphate produces a black precipitate of OsO_2. Stannous chloride produces a brown precipitate, soluble in HCl to a brown fluid.

This metal also forms amine bases, but not quite so markedly as is the case with either Pd or Rh. One has been described by Gibbs and Genth as $OsO_2Cl_2N_4H_{12}$. The formula given by Claus is

$$OsCl_24NH_3 + 2H_2O,$$
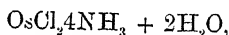
probably
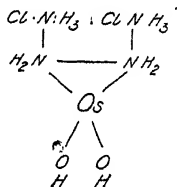
RUTHENIUM, Ru'', [iv], [vi], and [viii], also a pseudo-triad. Atomic weight, 101·7.—Found in small quantity only, in that portion of the platinum ores which remains behind after treating with aqua regia. It is a greyish white metal, closely resembling iridium, and very difficultly fusible, requiring a temperature of over 1800°. When heated in the air it becomes covered with bluish black ruthenic oxide, Ru_2O_3, insoluble in acids. When pure it is insoluble in acids, being scarcely acted upon by aqua regia; fusion with hydrogen potassium sulphate is even without action upon it.

It is attacked either by fusion with KHO and nitre, or potassium chlorate, and is converted thereby into potassium ruthenate, K_2RuO_4, a dark green mass, soluble in water to an orange-coloured fluid, which tinges the skin black, from separation of black ruthenic oxide. Acids (HNO_3) throw down the black hydroxide.

Or it may be rendered soluble by ignition with potassium chloride in a current of chlorine gas, being thus converted into potassium ruthenic chloride, $2KCl,Ru^{iv}Cl_4$.

Ruthenium forms several oxides, chlorides, &c., thus:

Ruthenious oxide.	. RuO	Ruthenious chloride .	.	$RuCl_2$
Ruthenic ,, .	. Ru_2O_3	Ruthenic chloride .	.	Ru_2Cl_6
Ruthenic dioxide .	. RuO_2	Ruthenic tetrachloride	.	$RuCl_4$
Ruthenic trioxide	. RuO_3	(known only in combination)		
(anhydride)				
Ruthenic tetroxide	. RuO_4			
(perruthenic anhydride)				
Ru_2O_7 (known only in combination)				

Reactions in Solution.

A solution of ruthenic chloride, Ru_2Cl_6, prepared by dissolving in HCl the ruthenic hydroxide, precipitated by nitric acid from a solution of potassium ruthenate, may be used. It forms an orange-yellow-coloured solution, which on heating is resolved into HCl and a hydrated oxide.

SH_2 produces at first no precipitate, but after some time the fluid acquires an azure-blue tint, and deposits brown ruthenic sulphide, Ru_2S_3. This reaction is very delicate and characteristic.

$(NH_4)_2S$ produces a brownish black precipitate, difficultly soluble in excess.

KHO precipitates black ruthenic hydroxide, $Ru_2(HO)_6$, insoluble in alkalies, but soluble in acids.

KCyS produces, in the absence of other platinum metals, after some time a red coloration, which gradually changes to purple-red, and, upon heating, to a fine violet tint (very characteristic).

Alkali chlorides produce in concentrated solutions crystalline glossy violet precipitates of the double chlorides, difficultly soluble in water, insoluble in alcohol. They are decomposed on boiling with water, with separation of black ruthenious oxychloride.

KNO_2 forms a double salt, $3KNO_2,Ru(NO_2)_3$, readily soluble in an excess of the alkali nitrite. On the addition of a few drops of colourless NH_4HS the solution assumes a splendid dark red colour, changing to brown, without precipitation of sulphide.

Metallic zinc produces at first a fine azure-blue coloration (owing to the reduction of Ru_2Cl_6 to $RuCl_2$), which subsequently disappears, ruthenium being deposited in the metallic state.

(B) *As sulphides, soluble in yellow ammonium sulphide :* Iridium, molybdenum, tellurium, selenium, and germanium.

IRIDIUM, Ir", iv, and vi, also as a pseudo-triad. Atomic weight, 193·0. Specific gravity : if melted, about 22 ; if precipitated, 15 to 16. —Found in platinum ores alloyed with platinum, chiefly, however, in combination with osmium, and left behind as a native alloy in the form of very hard, metallic-looking grains when the ore is treated with aqua regia. On account of its hardness, and consequent resistance to wear, it is used for protecting the points of gold pens. " Platinum " vessels employed in the refining and concentration of

H_2SO_4 are made of an alloy of platinum with iridium. Alloys of this metal with platinum can also be employed as "resistance" pyrometers.

In this condition, or when reduced at a red heat by hydrogen, from any of its compounds, it is insoluble in every acid. Fusion with acid potassium sulphate oxidises, but does not dissolve it (distinction from Rh). When fused with NaHO in a silver crucible with access of air, or with sodium nitrate, it is likewise oxidised, but the compound of Ir_2O_3 and sodium is only slightly soluble in water. By the action of aqua regia the latter is dissolved to a deep black liquid, containing the double chloride of iridium and sodium, $2NaCl,IrCl_4$. The same compound is also obtained when a mixture of the iridium powder and dry sodium chloride is heated in a glass or porcelain tube in a current of chlorine gas, and the residue dissolved out with water.

Iridium forms numerous compounds with oxygen, chlorine, iodine, sulphur, &c., in which the metal exists as a dyad, pseudo-triad, tetrad, or hexad, as will be seen from the following list:

Oxides.

Iridious oxide	IrO.
Iridic ,,	Ir_2O_3.
Iridic dioxide (most stable)	IrO_2.
,, hydroxide (bulky, indigo-coloured)	$Ir(HO)_4$.
,, anhydride (not known in the free state)	IrO_3.

Chlorides.	Iodides.	Sulphides.
$IrCl_2$.	Ir_2I_6.	IrS, greyish black.
Ir_2Cl_6.	IrI_4.	Ir_2S_3, brownish black.
$IrCl_4$.		IrS_2.

All iridium chlorides are capable of forming crystalline double chlorides with the chlorides of the alkali metals.

Reactions in Solution.

A solution of the double chloride of sodium and iridium, $2(NaCl),IrCl_4$, may conveniently be employed.

SH_2 first decolorises the iridium solution, with separation of sulphur and reduction of the $IrCl_4$ to Ir_2Cl_6, and finally precipitates brown iridic sulphide, Ir_2S_3.

$(NH_4)_2S$ produces the same precipitate, readily soluble in excess.

KHO or NaHO, added in excess, colours the solution greenish, and precipitates a little brownish black potassium double chloride. On heating the liquid with exposure to the air it acquires at first a reddish tint, which changes afterwards to azure-blue (distinction from Pt), and when evaporated to dryness and taken up with water a colourless solution is obtained, and a blue deposit of iridic dioxide is left undissolved.

KCl precipitates dark brown potassium iridic chloride, $2KCl,IrCl_4$, insoluble in a concentrated solution of potassium chloride.

NH_4Cl throws down from concentrated solutions a dark red powder, consisting of small octahedral crystals of the ammonium double chloride, $2NH_4Cl,IrCl_4$, insoluble in a concentrated solution of the precipitant.

Reducing agents, such as potassium nitrite, oxalic acid, ferrous sulphate, stannous chloride, mercurous nitrate, reduce this double salt (as well as the potassium double chloride), especially when in hot solutions, to the sesqui salt, e.g.:

$$2(2KCl,IrCl_4) + 4KNO_2 = 6KCl,Ir_2Cl_6 + 2KNO_3 + N_2O_3.$$
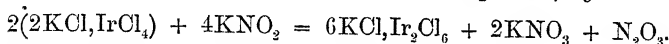
The double chloride crystallises out on cooling.

When $Ir(HO)_4$ is suspended in a solution of potassium nitrite, and the solution saturated with sulphurous acid and boiled, with renewal of the water, as long as SO_2 is given off, the whole of the iridium is converted into an insoluble brownish green iridic sulphite, $Ir(SO_3)_2,4OH_3$ (separation from Pt).

Metallic zinc precipitates black metallic iridium.

Iridium salts are reduced by alcohol in alkaline solutions to iridious compounds. Iridious compounds are soluble in HCl.

Iridium bases can be formed in a similar manner to those of other metals of this class.

$$IrN_2H_6Cl_2,$$
$$IrN_4H_{12}SO_4,$$
$$Ir_2(NH_3)_{10}(SO_4)_3,$$
$$IrCl_4NH_3 \quad \begin{cases} \text{In this the chlorine cannot} \\ \text{be detected by } AgNO_3, \end{cases}$$
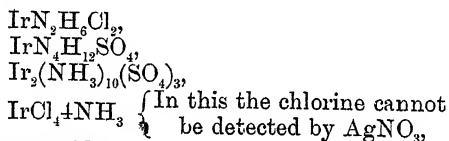
are types of some of these amides.

Some of the type $Ir_2(NH_3)_6$ are known.

MOLYBDENUM, Mo″, iv, vi, and viii, also a pseudo-triad. Atomic weight, 96·0. Specific gravity = 9·01.—Occurs only in a few minerals, more especially in molybdic disulphide (*molybdenite*, $Mo^{iv}S_2$, resembling graphite), and as lead molybdate (*wulfenite*, or yellow lead ore), $PbMoO_4$.

Molybdic anhydride, MoO_3, serves for the preparation of ammonium molybdate, a reagent largely used in the analysis of phosphates, and best obtained from molybdenite, by first roasting the ore, at a red heat, in an open vessel, and dissolving the impure anhydride in strong ammonium hydroxide. An acid ammonium molybdate, $(NH_4)_2Mo_2O_7 + OH_2$, crystallises out, on cooling, in large transparent crystals. The metal is prepared by intensely heating the oxide in a charcoal-lined crucible or by the aluminium reduction method. It is a silver-white, brittle, and exceedingly infusible metal. It is not affected by exposure to the air, but when heated it becomes first brown, then blue, and finally white, passing through various stages of oxidation until it is converted into molybdic anhydride, MoO_3.

Pure molybdenum files and polishes easily, and may be forged hot. It is not attacked by water containing CO_2 in solution.

Like iron, it dissolves carbon up to 3 per cent., forming a very hard compound.

From an iron-molybdenum alloy dilute acids remove the free iron and leave Fe_3Mo_2.

Molybdenum is insoluble in HCl, but is acted upon by HNO_3 or aqua regia, being converted into anhydride, if sufficient nitric acid be present.

It forms with oxygen, chlorine, sulphur, &c., compounds in which the metal exists as a dyad, pseudo-triad, tetrad, hexad, and octad, thus :

Oxides.	Chlorides.	Sulphides.
Molybdous oxide, MoO	$MoCl_2$	
Molybdic „ Mo_2O_3	Mo_2Cl_6	
= MoO,MoO_3	—	
Molybdic dioxide, MoO_2	$MoCl_4$	MoS_2 (the native molybdenite).
		Mo_2S_3.
Molybdic trioxide	—	MoS_3 (sulphomolybdic anhydride).
or anhydride, MoO_3	—	MoS_4 (per-sulphomolybdic anhydride).

There is some doubt about some of these oxides.

The higher oxide (anhydride) and sulphides form oxy and sulpho salts—molybdates and sulphomolybdates. Black molybdous hydroxide, $Mo(HO)_2$, forms with acids molybdous salts, which absorb oxygen readily from the air, and are powerful reducing agents. The principal salts are, however, the molybdates.

Dry Reactions.

Molybdic anhydride, when heated on charcoal in the outer flame, first melts, and is then partly volatilised and forms a yellow crystalline sublimate on the charcoal which turns white on cooling; in the inner flame it is reduced to the metallic state (even without Na_2CO_3); the metal can be obtained as a grey powder on levigating the charcoal. With borax all oxides of molybdenum give in the outer flame a bead which is yellow when hot and colourless on cooling; in the inner flame, a dark brown bead, which is opaque when excess of molybdenum has been used.

Reactions in Solution.

Employ a solution of ammonium molybdate.

The alkali molybdates are soluble in water. Most others are insoluble.

Nitric or hydrochloric acid precipitates white molybdic acid, H_2MoO_4, from a concentrated solution of a molybdate; soluble, however, in a large excess of the acid.

SH_2 gradually precipitates from acidulated solutions brownish black molybdic trisulphide, MoS_3, soluble in alkali sulphides or sulpho salts, which are decomposed again by acids with precipitation of MoS_3, especially on the application of heat. On the addition of a little SH_2 only, the molybdate

solution acquires at first a blue tint; added in larger quantities, it produces a precipitate, and the supernatant fluid appears green, till on the addition of excess of SH_2 the whole of the metal separates, though slowly, as a trisulphide.

$(NH_4)_2S$ gives a similar precipitate, soluble in excess.

Reducing agents, such as $SnCl_2$, $Hg_2(NO_3)_2$, Zn and HCl, &c., produce changes, marked by alterations in colour, to lower oxides.

The principal and *most characteristic reaction* for molybdic anhydride consists, however, in precipitating it in a nitric acid solution, as yellow phospho-molybdate, or arsenio-molybdate, by the addition of a mere trace of a soluble phosphate or arsenate.

TELLURIUM, Te″, ^{iv}, and ^{vi}. Atomic weight, 127·6. Melting-point, 452–455° C.—Occurs native in moderate quantities only (graphic and foliated tellurium); more often in combination with Au, Ag, Bi, Pb, as a (sulpho) telluride, analogous to sulphides, &c.; or as tellurous acid, in combination with metallic bases.

Tellurium exhibits all the physical properties of a metal, and resembles antimony in its general appearance. It is white, brittle, and readily fusible, and may be sublimed in a glass tube. When heated in the air it burns with a greenish blue flame, emitting thick white fumes of tellurous anhydride, TeO_2. It is insoluble in HCl, but dissolves readily in HNO_3, forming TeO_2, a white substance which fuses to a yellow fluid at a gentle heat, and volatilises on stronger ignition in the air. Tellurous anhydride scarcely dissolves in water, and the solution does not redden litmus; readily in HCl, less so in HNO_3. It also dissolves freely in alkalies, slowly in ammonium hydroxide, forming alkali tellurites. On dilution with water, white tellurous acid, H_2TeO_3, is precipitated from an acid solution. A nitric acid solution slowly deposits crystalline tellurous anhydride, even without the addition of water.

Tellurium forms several oxides, chlorides, sulphides, &c., in which the metal is a dyad, tetrad, or hexad; thus:

Oxides.

Tellurous oxide (anhydride) . . .	TeO_2
„ acid	H_2TeO_3
Telluric oxide (anhydride) . . .	TeO_3
„ acid	H_2TeO_4

Chlorides.

Tellurous, or dichloride	$TeCl_2$
Telluric, or tetrachloride . . .	$TeCl_4$

It also forms with hydrogen a gaseous compound (telluretted hydrogen or hydrotelluric acid), TeH_2 (analogous with SH_2 and SeH_2).

Tellurium dissolves in strong sulphuric acid, giving a beautiful pink solution.

Both the di- and tri-oxides are capable of forming with metallic substances basic salts called tellurites and tellurates. The alkali and alkaline earthy tellurites—formed by fusing tellurous acid with the carbonates of these metals—are all more or less soluble in water ; all others obtained by double decomposition are insoluble. The tellurates of the alkali metals, prepared in like manner, are also soluble in water ; the others are insoluble. They can be prepared by double decomposition.

The sulphides of this element act as sulpho acids, forming, with the alkali sulphides, sulpho-tellurites and tellurates.

Dry Reactions.

When tellurites or tellurates are heated with charcoal and K_2CO_3 they are reduced to potassium telluride, TeK_2, which produces a black stain on a moist silver plate, and is soluble in water, forming a dark red solution. When HCl is added to this solution hydrotelluric acid gas, TeH_2, is evolved, resembling SH_2 in smell, and soluble in water to a pale-red solution, which is decomposed in contact with air, with deposition of tellurium.

All compounds of tellurium are readily reduced on charcoal in the inner flame. The reduced element is volatilised and forms a white, scarcely visible deposit of tellurous anhydride on the charcoal. Stannous chloride colours it black, owing to the separation of tellurium.

With borax or microcosmic salt a clear, colourless bead is obtained, which, when heated on charcoal, is rendered grey and opaque, owing to reduced element.

Reactions in Solution.

(A) **TELLURIC COMPOUNDS.**—Use a solution of potassium tellurate, K_2TeO_4 (obtained by fusing potassium tellurite or tellurium with nitre).

> HCl does not decompose cold solutions of tellurates, but on boiling chlorine is evolved, and on dilution with water tellurous acid, H_2TeO_3, is precipitated, soluble only in a considerable excess of HCl. (Distinction of TeO_3 from TeO_2.)

(B) **TELLUROUS COMPOUNDS.**—Use a solution of potassium tellurite, K_2TeO_3.

HCl decomposes this solution and precipitates white tellurous acid. Tellurium resembles in this respect Sb and Bi compounds.

> SH_2 precipitates from acid solutions a brown substance, from which the sulphur can be easily extracted, resembling in colour SnS, and very freely soluble in ammonium sulphide.
>
> Reducing agents, e.g., Na_2SO_3, $SnCl_2$, metallic zinc or magnesium

and HCl, a solution of sulphurous acid, &c., reduce tellurium compounds and precipitate black tellurium, which is insoluble in an aqueous solution of potassium cyanide.

SELENIUM, Se$''$, ^{iv}, and ^{vi}. Varieties a and β. Atomic weight, 79·2. Specific gravity: $a = 4·8$; $\beta = 4·2$. Melting-point: $a = 217°$ C.; $\beta = 125-130°$ C. Boiling-point – 680°C., about.—Occurs in the free state at Culebras, Mexico, in crystals, sometimes called riolite, after Del Rio, who discovered it. It is also found in certain iron and copper pyrites, and where these are used for the manufacture of sulphuric acid a red deposit of selenium is found in the chambers; consequently it is often found in the sulphuric acid. It is found also as selenides of Pb, Cu, Hg, Ag, Fe, &c. Selenium, like sulphur, occurs in different allotropic states, amorphous and crystalline. The crystalline or a-selenium is insoluble in CS_2; β or amorphous selenium is soluble in CS_2.

Selenium conducts electricity slightly; exposure to light increases its conducting power; when heated its conducting power decreases. This remarkable property of selenium may probably be made use of for photometrical purposes.

Reactions.

Heated in air, it burns with a bluish flame and forms selenious anhydride, SeO_2, whilst at the same time a disagreeable odour is given off. The same oxide is formed when selenium is dissolved in nitric acid or aqua regia.

It combines directly with bromine and chlorine, and also when heated with iodine, sulphur, phosphorus, and metals.

It dissolves in strong sulphuric acid, forming a green solution, from which water precipitates the element as a red powder.

Selenites containing selenic anhydride, SeO_3, are formed by heating selenium or its compounds with carbonates and nitrates of the alkalies. These oxides form two series of salts, viz., selenites and selenates. The selenites are the more stable of the two.

Dry Reactions.

Selenium compounds are reduced, when heated with Na_2CO_3 on charcoal, in the inner blowpipe flame, and may be readily recognised by a characteristic odour which they give off. If the saline residue, which contains sodium selenide, Na_2Se, be placed on a bright silver coin and moistened with a drop of water, a black stain is produced on the silver. Treated with dilute HCl, it evolves gaseous hydroselenic acid (selenietted hydrogen), H_2Se, analogous in composition and properties to sulphuretted hydrogen. It is an inflammable, fœtid, poisonous gas, very soluble in water. The aqueous solution of H_2Se gradually deposits selenium on exposure to air; it precipitates selenides from solutions of many metallic salts. Selenium compounds impart a bright blue colour to the Bunsen flame.

Reactions in Solution.

(A) **SELENIC COMPOUNDS.**—Use a solution of potassium selenate, K_2SeO_4.

Selenates are stable salts, closely resembling the sulphates. They are soluble in water with the exception of the barium, strontium, calcium, and lead salts, which are insoluble in water and in dilute acids.

> HCl decomposes selenates on boiling; chlorine is evolved, and the salt is reduced to a selenite. (Distinction from SeO_2.)
>
> SH_2 does not produce a precipitate till the selenate has been reduced to selenite by boiling with HCl.
>
> $BaCl_2$ produces a white precipitate of barium selenate, $BaSeO_4$, insoluble in water and in dilute acids; decomposed by boiling with HCl.

(B) **SELENIOUS COMPOUNDS.**—Use a solution of an alkali selenite.

The normal alkali selenites are soluble in water, most others are insoluble; nearly all acid selenites are soluble. HCl dissolves but does not decompose selenites.

> SH_2 produces from an acid solution of a selenite a lemon-yellow precipitate of selenious sulphide, SeS_2 (?), which almost immediately breaks up into its component elements, $Se + S_2$, but is readily soluble in ammonium sulphide.
>
> $BaCl_2$ gives a white precipitate of barium selenite, $BaSeO_3$, soluble in dilute HCl or HNO_3.
>
> Reducing agents, such as SO_2, alkali sulphites, $SnCl_2$, metallic Zn, and Fe, precipitate selenium from acidulated (HCl) solutions, as a red powder, which turns grey at high temperatures and is soluble in KCy solution. ($FeSO_4$ is without action.) Metallic copper is immediately coated black when placed in a warm solution containing hydrochloric acid, and on standing the solution turns light red, from separation of amorphous selenium.

Test for Se in H_2SO_4.—Five parts of the acid when diluted with ten parts water, and an equal volume of a saturated solution of SO_2 added, gives a red precipitate of Se.

GERMANIUM, Ge″, and ⁱᵛ. Atomic weight, 72·5. Specific gravity, 5·47.—This metal was discovered by C. Winckler in *argyrodite*, which is a sulphogermaniate of silver.

The metal is silvery white and brittle; it melts at about 900° C., and volatilises at a little higher temperature. Dry chlorine combines with the metal and forms $GeCl_4$, a colourless liquid that boils at 86° C., fumes in the air, and is decomposed by water. HNO_3 acts on the metal and gives a white oxide; H_2SO_4 dissolves it, and by evaporation of the solution and ignition of the residue GeO_2 is obtained; HCl is without action upon the metal.

GeO is a greyish black powder, soluble in HCl. This solution of germanous chloride gives a yellow precipitate with alkalies, a white precipitate with K_4FeCy_6, and a reddish brown precipitate with H_2S. It reduces permanganates and gold and mercury salts.

Acid·solutions of GeO_2 give a white, precipitate of GeS_2 by the action of SH_2. The precipitate is soluble in ammonium sulphide.

REACTIONS OF THE RARE METALS OF GROUP I.

Group I. comprises the rare metals precipitable by HCl—viz., the metal tungsten, or wolfram, which is precipitated as tungstic acid, H_2WO_4, and thallium, precipitated as thallous chloride, TlCl. Several other metals already treated of in Group III. besides thallium, viz., columbium, tantalum, molybdenum, are likewise precipitated, but the precipitated acids ($HCbO_3$, $HTaO_3$, and H_2MoO_4) dissolve again in an excess of hydrochloric acid.

TUNGSTEN or **WOLFRAM**, W^{iv} and ^{vi}. Atomic weight, 184.— This metal occurs in nature as trioxide combined as tungstates, in combination with the bases CaO, FeO, MnO, in the minerals wolfram, $Fe''(Ca)WO_4$, and $CaWO_4$, scheelite, &c.

The metal can be obtained by intensely heating the oxide in a current of hydrogen, or combined with some carbon by fusion in the electric furnace; also by reduction of tungstic oxide with aluminium powder. It forms an iron-grey powder, of specific gravity 19·12, very difficultly fusible, and becomes again oxidised to tungstic anhydride, WO_3, when heated in air. The fused or partly fused product obtained by reduction with Al powder is not oxidised by air. Most self-hardening steels, now so largely used, contain a fair proportion of tungsten. On treatment of these with dilute acids the compound Fe_3W remains as an insoluble powder. Dry chlorine gas converts tungsten into dark violet WCl_6, which sublimes, and a more volatile red compound, WCl_4. Both chlorides are decomposed by water into the corresponding hydroxides, with formation of HCl. The metal is insoluble, or nearly so, in acids, even in aqua regia.

The following are some of the more important compounds which tungsten forms with oxygen, chlorine, and sulphur:

	Oxides.	Chlorides.	Sulphides.
Tungstic anhydride (lemon-yellow) . .	WO_3	WCl_6	WS_3
Tungstic dioxide (brownish black) . .	WO_2	WCl_4	
Intermediate (blue-coloured) oxide .	W_2O_5	WCl_5	
	$= WO_2, WO_3$	WCl_4, WCl_6.	

Tungstic anhydride can be prepared from wolfram or tungsten by digesting the finely divided mineral in aqua regia, till it is completely decomposed, and evaporating to dryness on a water-bath. The metallic chlorides are dissolved out with acidulated water, and the residue, which contains a little silica and sometimes columbic

APPENDIX II.

ORGANIC ACIDS, &c.

ALL organic acids other than the hydrocyanic acids contain at least one negative group or complex, containing a replaceable hydrogen atom, of the form —CO.OH (carboxyl), the molecule of
which, $\begin{matrix} OC.OH \\ | \\ OC.OH \end{matrix}$, constitutes oxalic acid, a substance resulting from
the oxidation of a large number of organic substances—*e.g.*, sugar, woody fibre, &c.—by the action of powerful oxidising agents, and is, on further oxidation, itself resolved into the products of the final oxidation of everything organic, viz., carbon dioxide and water. This group,—COOH, is considered to be characteristic of organic acids.

A high temperature breaks up nearly all salts of organic acids. Those of alkali and alkaline earthy bases leave upon gentle ignition carbonates, with separation of carbon, and consequent blackening, oxalates perhaps excepted. The residue, with the exception of the carbon, being soluble in water, indicates that the organic acid was combined with alkali metals, and if insoluble, with alkaline earthy bases. The decomposition is, moreover, accompanied in most instances by the evolution of volatile matter, of carbon monoxide, hydrocarbons, acetone, and other products. Some metallic salts leave metal or oxide.

In the free state organic acids are either volatile, and can be distilled or sublimed, generally without undergoing decomposition and without leaving any carbonaceous residue—as, for instance, formic, acetic, benzoic, and many others. Most of these acids can be displaced from their compounds by mineral acids, as sulphuric. Some organic acids are non-volatile, and are decomposed on heating alone, leaving generally a residue of carbon. Many of these acids will, however, distil in a current of steam without decomposition. Some are also more soluble in liquids, as ether, chloroform, petroleum, than in water, and may be by these means separated.

FORMIC ACID, $O : \begin{matrix} H \\ \dot{C}.OH \end{matrix}\Big\}$ exists in many plants, and can be exuded under certain conditions by some animals—for instance, ants. It can be obtained by the oxidation of methyl alcohol, $CH_3.OH$, by platinum black.* The action of glycerine on oxalic acid gives one of

---

* This method is of interest as showing its constitution and its relation to the alcohols and carbinols, of which CH_3OH is the simplest, as is formic the simplest organic or carboxylic acid.

The experiment may be performed in a flask with wide neck. A few

the easiest methods of obtaining formic acid in quantity. The reaction takes place in several stages, glycerol monoformin being one. Equal weights of the two substances are heated together in a retort to 100° C., when the formic acid distils over with the water. Dry formic acid is a liquid above 8·5° C.; it boils at 99° C., and has a specific gravity of 1·22. It is monobasic. Oxidising agents convert it into CO_2 and OH_2. Its salts give the same reactions.

Dry Reactions.

Formates of the fixed alkalies and alkaline earthy bases, when heated out of contact with air, are decomposed into carbonates, and a little carbon, with disengagement of combustible gases—mainly carbon monoxide and hydrogen. Formates of the heavy metals give off CO_2, CO, and OH_2, leaving the metal (generally mixed with a little carbon).

Reactions in Solution.

A solution of sodium formate, $\overset{H}{OCONa}$, gives the reactions.

All formates are soluble in water, lead formate least so; some also in alcohol.

Formic acid and formates are readily recognised by their property of reducing salts of the noble metals, e.g., $AuCl_3$, $AgNO_3$, $Hg_2(NO_3)_2$, or $HgCl_2$, to the metallic state, with evolution of carbon dioxide.

Mercuric chloride solution warmed with a little formic acid or formate and HCl gives a white precipitate of Hg_2Cl_2—

$$2HgCl_2 + HCOOH = Hg_2Cl_2 + CO_2 + 2HCl.$$
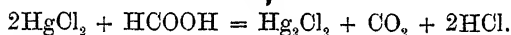
On boiling, the reaction goes further, and Hg is formed.

This reducing action distinguishes formic acid from acetic acid and some of its homologues.

Potassium permanganate is rapidly deoxidised by formic acid.

Formic acid or a formate, when heated with a solution of potassium dichromate and sulphuric acid, is broken up, with evolution of CO_2.

When heated with concentrated sulphuric acid, formic acid and formates are broken up into water and carbon monoxide, which latter burns with a blue flame. (Method of preparing carbon monoxide gas—see ante.) The mixture does not blacken.

$$HCOOH - H_2O = CO.$$
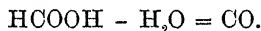
Formic acid may be synthetised by heating carbon monoxide and KHO to about 100° C.: $KHO + CO = KOOCH$; or moist soda-lime to 190–200°; also from HCN by the action of KHO, thus:

---

c.c. of methyl alcohol are introduced, and then a red-hot platinum wire spiral lowered into the flask, not touching the alcohol; the wire continues to glow, and some formic aldehyde, HCOH, is first produced. Some of this oxidises further, producing HCOOH. The residue in the flask will be found to be acid to litmus.

$$HCN + \begin{Bmatrix} H_2O \\ KOH \end{Bmatrix} = H.C\begin{matrix} O \\ OK \end{matrix} + NH_3.$$
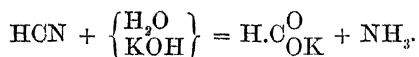
Formic acid heated with excess of zinc gives CO and H.

ACETIC ACID, $\begin{matrix} CH_3 \\ OC.OH \end{matrix}$—Is obtained either by the oxidation of alcohol, thus :

$$\begin{Bmatrix} CH_3 \\ CH_2OH \end{Bmatrix} + O_2 = \begin{matrix} CH_3 \\ OC.OH \end{matrix} + OH_2,$$
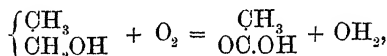
or by the destructive distillation of vegetable substances, especially of wood, and organic acids containing much oxygen. The acid can be synthetised in several ways—*e.g.*, by the hydrolysis of methylcyanide with KHO; from sodium methyl, CH_3ONa and CO at $160° =$ NaOOCCH$_3$, and others. Chromic acid, or permanganate, will oxidise alcohol to acetic acid, but in almost every case of oxidation some aldehyde is first formed.

In the ordinary method of preparation the oxidation of the alcohol is carried on by the agency of a bacterium, which can function in very dilute alcohol solution. It practically conveys atmospheric oxygen to the alcohol.

The main source of commercial acetic acid is the liquid distillate obtained during wood-charcoal making, the woody matters being charred in iron vessels and the volatile matters carefully condensed.

Pure anhydrous acetic acid boils at $118°$ C. This is termed glacial acetic acid, and is prepared by decomposing dry sodium acetate (5 parts by weight) with concentrated sulphuric acid (6 parts by weight) and distilling. The crude acid is placed over MnO_2, in order to remove any SO_2, and rectified by distillation over a little dry sodium acetate. It easily crystallises when nearly pure.

Dry Reactions of Acetates.

Acetates are decomposed when distilled in a retort or similar partially closed vessel, yielding an inflammable volatile liquid, acetone, along with water and small amounts of CO, CO_2, and sometimes CH_4, &c.

$$\begin{matrix} CH_3 \\ OCO \\ OCO \\ CH_3 \end{matrix} \!\!\!> Ca = CaCO_3 + \begin{matrix} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{matrix}$$
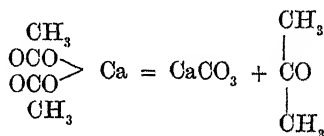
Calcium acetate.   Acetone.

The acetates of the alkalies and alkaline earthy bases, when strongly heated in the air, leave a carbonate; those of the heavy metals leave either a metallic oxide, or the metal itself, mixed with carbon. Thus,

$$2(AgO_2CCH_3) = 2Ag + (CH_3CO_2)_2O + O;$$
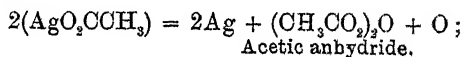
Acetic anhydride.

is the action with silver acetate.   Some acetic anhydride is produced, and the oxygen may, instead of coming off as such, oxidise some of the acetic molecule to CO_2 and H_2O.

Heated with alkali hydroxides, dry sodium acetate, and most other acetates, give off marsh-gas, or methane, CH_4, thus:

$$\begin{matrix} CH_3 \\ OCONa \end{matrix} + NaHO = Na_2CO_3 + CH_4.$$
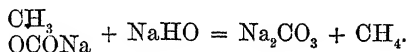
The gas can be collected in the usual manner over water, and on applying a light it burns quietly with an almost non-luminous flame to water and carbon dioxide.   It generally contains a little hydrogen, and traces of acetone.

Reactions in Solution.

A solution of sodium acetate may be employed.

All acetates are soluble in water.   Silver and mercurous acetates are the least soluble.

On heating a solid acetate (or a concentrated aqueous solution of one) with alcohol and concentrated sulphuric acid, acetic ether (ethylic acetate), $CH_3C.O.OC_2H_5$, is formed, which possesses a fragrant odour. The change is expressed thus:

$$CH_3COONa + C_2H_5OH + H_2SO_4 = \begin{cases} CH_3 \\ C.O.OC_2H_5 \end{cases} + HNaSO_4 + OH_2.$$
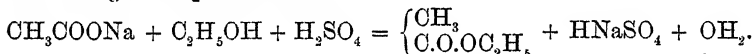
Too much alcohol should be avoided, lest common ether, $O(C_2H_5)_2$, be formed, the odour of which would mask that of the acetic ether. Excess of sulphuric acid is advisable.   Acetates of a dibasic metal like Ca or Ba, when heated alone in a retort or similar closed vessel, yield more acetone than an alkali acetate, where much CH_4 accompanies the acetone.

By distilling an acetate with moderately dilute sulphuric acid in a retort, free acetic acid is obtained, which is recognised by its characteristic pungent odour.   Acetic acid is not easily oxidised by chromic acid when very pure, or glacial, more easily when dilute, but still not rapidly.

Fe_2Cl_6 added to a solution of an acetate produces a deep red-coloured solution, owing to the formation of ferric acetate.   On boiling, the whole of the iron is precipitated as basic ferric acetate, in the form of brownish yellow flakes. NH_4OH precipitates the iron from a solution of ferric acetate as ferric hydroxide.

Ammonium acetate, with ammonium hydroxide, dissolves several insoluble sulphates—e.g., $PbSO_4$, $CaSO_4$.

Ammonium acetate on being heated in a retort decomposes, giving off water and leaving acetamide, a compound having a characteristic odour, something like mice excrement, which contains it.

$$CH_3COONH_4 = H_2O + CH_3.CO.NH_2.$$

Dry acetates heated with arsenious oxide, As_2O_3, give cacodyl, CH_3AsCH_3, readily distinguished by its onion-like odour.   It is

highly poisonous.   This reaction, if performed at all, should only be done on the smallest scale.

Approximate Separation of Acetic Acid from its next higher Homo- logues.[*]—Add enough potassium or sodium hydroxide to convert the acetic acid into acetate, and distil.   The acid containing the least number of carbon atoms, being the stronger, is first neutralised, and, if sufficient alkali has been added, the distillate is obtained free from acetic acid.

OXALIC ACID, $\begin{cases} COOH \\ COOH \end{cases}$—" Dicarboxyl."—Exists   in   rhubarb, sorrel, and other plants in the form of acid salts, and may be obtained by the oxidation of a large number of organic substances— *e.g.*, sugar, by nitric acid ; or woody fibre, by the action of melted caustic alkalies.   The free acid is a violent poison.   It crystallises in rhombic prisms with two molecules of water of crystallisation, which it loses when exposed to dry air—*i.e.*, it effloresces and crumbles to a powder.   With bases it forms an important series of salts, called oxalates.   The acid being dibasic, two series of salts, neutral and acid, $\dfrac{OCOK}{OCOK}$ and $\dfrac{OCOK}{OCOH}$, exist, besides some super acid oxalates.

Oxalic acid may be looked upon as the hydrate of the unknown oxide of carbon, C_2O_3.   An oxide of this composition has recently been obtained.

Dry Reactions.

Oxalic acid when heated by itself loses its crystal water, and then sublimes for the most part unchanged ; a portion of it breaks up into CO, CO_2, and some formic acid.   Oxalates yield, upon ignition, different products of decomposition, according to the nature of the base contained therein.

Alkali oxalates leave a carbonate, with slight blackening, and give off carbon monoxide.

Alkaline earthy oxalates leave a carbonate, together with some caustic base, if a strong heat be applied, and give off CO and CO_2.

Oxalates containing metallic bases which do not form carbonates, or the carbonates of which are decomposed by heat, break up into metallic oxides, and give off equal volumes of CO and CO_2, or into metal—as, for instance, silver oxalate, which gives off CO_2.

Heated with strong H_2SO_4, oxalates and the acid decompose into CO_2 and CO, which escape together.

Reactions in Solution.

Use a solution of ammonium oxalate.

Beside the alkali normal oxalates very few are soluble in water. Mineral acids dissolve the insoluble oxalates by forming perhaps acid oxalates.

* Homologues of acetic acid are propionic, CH_3CH_2COOH butyric $CH_3CH_2CH_2COOH$, and so on.   They differ from acetic by containing nCH_2 more in the molecule.   Otherwise their basicity and general properties are very much the same.

Any soluble calcium salt precipitates even from very dilute solutions white pulverulent calcium oxalate, readily soluble in hydrochloric or nitric acid; almost insoluble in oxalic or acetic acid, and in potassium or ammonium hydroxide. Heat promotes the precipitation from very dilute solutions. This constitutes one of the most delicate reactions for oxalic acid.

$BaCl_2$ gives from solutions of neutral oxalates a white precipitate of barium oxalate, soluble in oxalic acid, readily soluble in hydrochloric or nitric acid.

$AgNO_3$ produces a white precipitate of silver oxalate, $\begin{matrix} COOAg \\ | \\ COOAg \end{matrix}$, soluble in dilute nitric acid, and in ammonium hydroxide.

Concentrated sulphuric acid decomposes oxalic acid or oxalates, on warming only, into CO and CO_2, without blackening, by withdrawing from the molecule of oxatyl a molecule of OH_2. The gaseous mixture is passed through a wash-bottle containing sodium hydroxide or lime-water, and the carbon monoxide gas collected over water. (Usual method for preparing carbon monoxide.)

Oxalic acid or oxalates in the presence of free mineral acids act as reducing agents.

Treat a little black oxide of manganese and oxalic acid, or an oxalate, with a few drops of concentrated sulphuric acid. Effervescence ensues. The gas which escapes is carbon dioxide, resulting from this reaction :

$$MnO_2 + \begin{matrix} OCOK \\ OCOK \end{matrix} + 2H_2SO_4 = 2CO_2 + MnSO_4 + K_2SO_4 + 2OH_2.$$
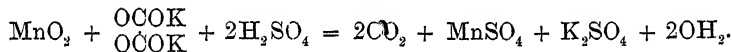
A solution of gold is reduced to metallic gold, thus :

$$2AuCl_3 + 3\begin{matrix} OCOH \\ OCOH \end{matrix} = 6CO_2 + Au_2 + 6HCl.$$
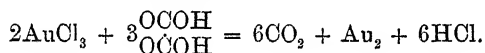
Potassium permanganate is speedily reduced (decolorised). The free acid dissolves in alcohol, both hot and cold, but not in chloroform or benzene.

Some of the cerite metals, as cerium, lanthanum, didymium, give oxalates *insoluble* in moderately strong HCl.

TARTARIC ACID, $\begin{matrix} OC.OH \\ HCOH \\ HCOH \\ OCOH \end{matrix}$ —This acid is dibasic. It is found in grapes, tamarinds, pine-apples, and several other fruits in the form of hydrogen potassium tartrate. The acid met with in commerce is prepared from the tartar or argol, an impure hydrogen potassium tartrate, deposited from the grape juice during fermentation. The acid forms colourless transparent crystals, very soluble in water, both hot and cold, and soluble also in alcohol. The aqueous solution undergoes gradual decomposition. There are five modifications of tartaric acid, due to structural differences in the molecule.

Dry Reactions.

Tartaric acid is decomposed by heat, giving off an odour resembling that of burnt sugar (caramel), and leaving a residue of carbon. Alkali tartrates when heated in a test-tube are decomposed, with evolution of inflammable gases, leaving a mixture of finely divided charcoal and carbonate (black flux), from which the carbonate may be extracted by water. The carbonaceous residue left upon igniting alkaline earthy tartrates contains an insoluble carbonate, and effervesces when treated with dilute hydrochloric acid. Tartrates of the heavy metals also undergo decomposition, accompanied by the characteristic odour of burnt sugar, and leave much carbon mixed with metallic oxide or metal.

Reactions in Solution.

Use a solution of tartaric acid, and for some reactions a solution of a normal salt, as Rochelle salt, potassium sodium tartrate.

The alkali tartrates are soluble in water, the acid salts less so than the neutral tartrates. The normal tartrates of the alkaline earthy bases, of the earths and heavy metals, are difficultly soluble in water, but dissolve readily in dilute tartaric acid. Alkalies fail to precipitate double tartrates containing an alkali and metallic base. Hence the presence of tartaric acid serves to prevent the precipitation of Fe_2O_3, Cr_2O_3, ZnO, NiO, CoO, MnO, CuO, PbO, Bi_2O_3, PtO_2, or CdO, whilst some other substance, $e.g.$, phosphoric acid, if present, may be precipitated from an alkaline solution.

KCl (or other potassium salt, especially a very soluble one) produces in a solution of free tartaric acid a heavy white crystalline precipitate of hydrogen potassium tartrate, readily soluble in mineral acids and in alkalies and alkali carbonates, insoluble in acetic acid. The precipitation is accelerated by agitation and by allowing to stand for some hours. Alkalies dissolve the precipitate, forming a normal tartrate, soluble in water, from which acetic acid reprecipitates the acid salt.

$Ca(HO)_2$ added in excess to free tartaric acid precipitates white calcium tartrate.

$CaCl_2$ (but not $CaSO_4$, except on long standing) precipitates from a solution of a normal tartrate white calcium tartrate, soluble in acids, even tartaric acid, in ammonium salts, but not in ammonium hydroxide. The precipitate, especially as long as it is amorphous, $i.e.$, recently precipitated, is soluble in cold potassium or sodium hydroxide, when nearly free from carbonate, but is reprecipitated on boiling as a gelatinous mass which redissolves on cooling.

$AgNO_3$ produces from a solution of a normal tartrate ($e.g.$, Rochelle salt) in the cold a white curdy precipitate of silver tartrate. On filtering and dissolving some of the precipitate off the filter with a little dilute ammonium hydroxide, and heating the solution in a clean test-tube or flask during ten or twenty minutes, in water, heated to about 66° C., the glass becomes coated with a fine silver mirror.* (Characteristic reaction for tartaric acid.)

* The presence of a little free NaHO or KHO accelerates the formation of the silver mirror.

Lead acetate gives a white crystalline precipitate of lead tartrate from solutions of tartaric acid or its soluble salts. The precipitate is soluble in nitric acid and in ammonium hydroxide; the latter giving rise to the formation of lead ammonium tartrate, which cannot be precipitated by ammonium hydroxide.

Tartaric acid and ammonium hydroxide dissolve lead sulphate.

Concentrated H_2SO_4 decomposes tartaric acid, or a tartrate, on heating, with evolution of SO_2, CO_2, and CO, and separation of carbon.

CITRIC ACID, $\begin{array}{c} OH \\ HC.CO.OH \\ HC.CO.OH \\ H_2C.CO.OH \end{array}$ —Tribasic.—Obtained from orange or lemon juice. Found also in many other fruits. It forms colourless prismatic crystals, which possess a pure and agreeable acid taste. They dissolve in cold and hot water, and in alcohol. The aqueous solution undergoes decomposition after a time. The citrates are very numerous, the acid forming, like phosphoric acid, three classes of salts by the replacement of one, two, or three atoms of hydrogen by an equivalent amount of a metal. There are no absolutely insoluble citrates.

Dry Reactions.

On heating citric acid, it loses first its water of crystallisation, then fuses, and is decomposed with disengagement of pungent and irritating acid fumes into aconitic acid, and finally to citraconic anhydride, leaving a less abundant carbonaceous residue than tartaric acid. Alkali and alkaline earthy citrates leave a carbonate upon ignition.

Reactions in Solution.

Use a solution of citric acid in water, or a solution of a normal alkali citrate.

Potassium salts give no precipitate.

$Ca(HO)_2$ gives no precipitate from a cold solution of citric acid, or of a neutral citrate; but on heating a white precipitate of calcium citrate is obtained. (Distinction between tartaric and citric acid.) When both citric and tartaric acid are present the precipitate produced by $Ca(HO)_2$ or $CaCl_2$ in the cold solution is filtered off, and the clear filtrate boiled, when a further precipitate indicates citric acid.

$CaCl_2$ produces at first no precipitate in a cold aqueous solution of citric acid, or a soluble citrate; but on standing precipitation takes place, and is all but completed, even in the cold, after twenty-four hours. On boiling a white precipitate of calcium citrate is obtained if the solution be neutral, or if it contain an excess of lime-water or ammonium hydroxide. This precipitate is insoluble in sodium or potassium hydroxide, but soluble both in ammonium salts and in acids.

Silver nitrate dissolved in ammonium hydroxide does not form a mirror upon heating, but a black deposit takes place after boiling for some time. Citric acid, like tartaric acid, prevents the precipitation of certain oxides, especially of Al_2O_3, Fe_2O_3, of Groups II. and III. and some phosphates by caustic alkalies, on account of the formation of soluble double citrates, containing an alkali base and a heavy metal.

Concentrated sulphuric acid decomposes citric acid or citrates slowly. On cautiously applying heat CO and CO_2 escape, at first without any blackening of the liquid, but on boiling for some time SO_2 is evolved and carbon separates.

SUCCINIC ACID, $\begin{cases} COOH \\ C_2H_4 \\ COOH \end{cases}$.—This acid is an ethylene . dicarboxylic

acid, and may be made from ethylene, C_2H_4, through the bromide, $C_2H_4Br_2$, and cyanide, $C_2H_4(CN)_2$, and hydrolysis of this. It is obtained by the distillation of amber, of fossil resin, and also by the long-continued action of nitric acid upon butyric, stearic, or margaric acids, by fermentation of sugar, malic acid, glycerine, &c. The acid crystallises in white plates, is readily soluble in water, alcohol, and ether, and is not acted upon by boiling nitric acid. Heated in a tube open at both ends, it sublimes in silky needles. Heated upon platinum foil, it burns with a blue flame and without smoke. It melts at 180° C., but gives off fumes at 130° C. At 235° C. it boils and forms the anhydride.

Succinates are decomposed upon ignition; the alkali and alkaline earthy succinates leave a carbonate mixed with carbon.

Most succinates are soluble in water.

Lead acetate gives a white precipitate of neutral lead succinate, $\begin{cases} CO-O \\ C_2H_4Pb, \\ CO-O \end{cases}$ which is rendered basic by treatment with ammonium

hydroxide.

Fe_2Cl_6 produces from a solution of neutral ammonium succinate a brownish red, voluminous precipitate of basic ferric succinate, $(C_4H_4O_4)_3Fe_2,Fe_2O_3$, readily soluble in mineral acids. NH_4OH renders the precipitate darker by withdrawing a quantity of saccinic acid as ammonium succinate, leaving a more basic succinate. (This reaction serves for the separation of Mn″ from Fe‴.)

On boiling the precipitate produced by ferric chloride from a solution of a succinate or benzoate, with ammonium hydroxide, soluble ammonium salts of these acids are obtained, which can be separated by filtration from the insoluble residue. On the addition of alcohol and $BaCl_2$ to the ammoniacal solution, a white precipitate of barium succinate is obtained, whilst benzoic acid gives no precipitate (distinction between benzoic and succinic acids).

Succinic acid is insoluble in chloroform. Benzoic is soluble. Magnesium benzoate is also soluble in alcohol, but the corresponding succinate is not.

BENZOIC ACID, $C_6H_5.CO.OH$.—Is found in many gums and balsams, from which it is obtained by sublimation. Heated in a tube open at both ends, the acid sublimes in long needles, giving off a pleasant smelling but irritating vapour. Heated on platinum foil, benzoic acid burns with a luminous, smoky flame.

The acid is very slightly soluble in cold water, 200 parts cold, 12 parts boiling. It is readily soluble in alcohol, ether, &c. Benzoates of tetrad metals are mostly insoluble in water; all others are soluble.

Fe_2Cl_6 gives a pale yellow precipitate of basic ferric benzoate, $(C_6H_5CO_2)_6Fe_2.Fe_2O_3 + 15OH_2$; and ammonium benzoate is employed sometimes for the separation of Fe''' from Mn''.

On distilling benzoic acid or benzoates with lime or baryta, benzene, C_6H_6, is obtained—

$$\left\{ {C_6H_5 \atop CO.OH} \right. + CaO = C_6H_6 + CaCO_3,$$
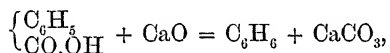
which may be made into nitrobenzene by HNO_3, and this into aniline. (See "Benzene.")

Dilute acids precipitate benzoic acid from aqueous solutions of benzoates; dilute nitric acid is without action upon the acid itself.

Heated with concentrated sulphuric acid, benzoic acid does not blacken, neither does it evolve SO_2.

Vapour of benzoic acid passed over heated zinc dust in a tube gives odour of bitter almonds, benzoic aldehyde, $C_6H_5.COH$. Also when a solution of a benzoate is acidified with H_2SO_4 and a piece of Mg immersed therein the same odour is produced.

Benzoic acid is "phenyl" formic acid. C_6H_5 functions in the place of H in formic acid.

SALICYLIC ACID, $C_6H_4 {.OH \atop .OCOH}$, exists in nature in combination with methyl alcohol in oil of winter-green (*Gaultheria procumbens*), and in saligenin, contained in willow-bark, &c. It may also be formed by heating the ortho-haloid benzoic acids with KHO.

$$C_6H_4.Br.COOH + 3KHO = C_6H_4(OK)COOK + KBr + 2H_2O.$$
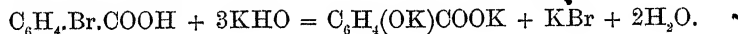
It is made on a large scale by Kolbe's reaction—that is, heating sodium phenol in CO_2 to 190° C. Phenol distils, and sodium salicylate remains in the retort.

$$2(C_6H_5.ONa) + CO_2 = C_6H_4ONaCOONa + C_6H_5OH.$$
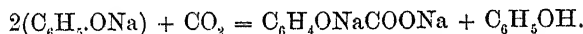
Salicylic acid is monobasic; it dissolves slightly in cold water, more easily in hot, in alcohol and ether. It melts at 156° C., and distils in steam. Its aqueous solution gives a fine violet coloration with Fe_2Cl_6. This colour is destroyed by mineral acids and by alkalies. 1 part in 100,000 OH_2 is indicated by this test. It is a powerful antiseptic.

On distilling salicylic acid with excess of lime phenol is produced.

$$C_6H_4{OH \atop COOH} + CaO = CaCO_3 + C_6H_5OH.$$

Salicylic acid.   Lime.   Calcium   Phenol.
carbonate.
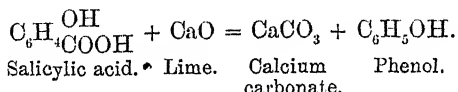
$AgNO_3$ and lead acetate give white precipitates with salicylates, but not with the free acid.

Bromine water added to solutions of salicylic acid gives a white crystalline precipitate of tribromsalicylic acid, similarly to phenol.

With Millon's reagent a similar red colour is produced to that with phenol.

ALCOHOL, $C_2H_6O = C_2H_5OH$. Specific gravity, 0.7939 at $15.5°$. Boiling-point, $78.4°$ C. at normal pressure.—Alcohol is a transparent, colourless, very mobile liquid, which readily dissolves resins, ethers, fats, essential oils, &c. It mixes with water and ether in all proportions. Its vapour is very inflammable, burning in the air with a blue flame only very slightly luminous and yielding water and carbon dioxide, and when mixed with air explodes by contact with a flame or by the electric spark.

When the vapour of alcohol mixed with air comes in contact with platinum black imperfect combustion takes place, the metal being generally heated to redness and the alcohol partly converted into aldehyde, acetic acid, formic acid, acetal, &c.

Strong nitric acid decomposes alcohol. Part of the nitric acid forms nitrate of ethyl, but the greater part is reduced to nitrous acid, which then forms nitrite of ethyl. At the same time many other compounds are formed, and the action may become explosive unless the materials are pure and used in small bulk only.

Strong sulphuric acid mixes with alcohol, producing considerable evolution of heat; with formation of ethyl hydrogen sulphate. Potassium and sodium act upon alcohol, with formation of ethylates and evolution of hydrogen ;

$$2C_2H_5OH + K_2 = H_2 + 2C_2H_5OK.$$

A good test for alcohol depends on the production of iodoform, although it is not the only substance which gives this test. It is best performed by warming the liquid to be tested, adding a solution of sodium carbonate, and then small crystals of iodine, until a slight brown coloration remains. On cooling the solution pale yellow flaky crystals of CHI_3 will fall out. They have a very characteristic odour.

Alcohol may be also very readily oxidised to aldehyde, and then to acetic acid, by any oxidising mixture, such as potassium dichromate and sulphuric acid, or potassium permanganate. A liquid containing alcohol when warmed with a strong $K_2Mn_2O_8$ solution causes a black or brown precipitate of MnO_2 and potassium acetate, which remains in solution, and may be tested for.

Aldehyde, CH_3COH, is formed when alcohol is oxidised with

potassium dichromate and sulphuric acid. The alcohol should be dropped in small quantities only at a time into the acid mixture, contained in a retort provided with condenser. The acid mixture should be warm, so that the aldehyde distils over as fast as formed, otherwise the action may be dangerous. It is a very volatile liquid, boiling at 21° C., and soluble in water, alcohol, and ether. It absorbs oxygen from air, and reduces silver and other salts, the metals being precipitated. With ammoniacal silver solution it gives a mirror of silver.

Methyl alcohol, CH_3OH, gives $CHOH$, formaldehyde, or "formalin," on oxidation. This stage of oxidation is attained when platinum black or hot platinum wire is held in a mixture of air and methyl alcohol vapour. (See Formic Acid.)

ETHER, $C_4H_{10}O = C_2H_5OC_2H_5$. Specific gravity, 0·736 at 0° C.— Pure ether is a very mobile, colourless liquid, of penetrating odour and sweet taste. On account of its low boiling-point, 35° C., it evaporates very rapidly at ordinary temperatures, causing thereby a great reduction of temperature. It mixes in every proportion with absolute alcohol, but not with water; 1 part of ether requires about 9 parts of water for solution, and itself dissolves about $\frac{1}{11}$ of its weight of water. It dissolves sulphur, phosphorus, iodine, &c., and is one of the best solvents for fats, oils, resins, and other organic substances.

Its vapour is very inflammable. It burns with a luminous flame. A mixture of its vapour and air is violently explosive.

By incomplete oxidation or imperfect combustion it is converted into aldehyde and acetic acid. It is not attacked by sodium or potassium, but energetically by chlorine. The reaction is most violent with chlorine and its vapour. Bromine acts less violently.

Dry ether mixes to a clear liquid with sulphide of carbon; a slight trace of water causes a milkiness.

CHLOROFORM, $CHCl_3$.—Is a colourless liquid, of specific gravity 1·62, boiling at 61° C. It is soluble in about 200 times its weight of water, but to any extent in alcohol, ether, CS_2, &c. It is an excellent solvent for oils and fats, resins, &c.

Chloroform heated with Fehling's alkali copper tartrate solution produces Cu_2O.

$$CHCl_3 + 5KHO + 2CuO = Cu_2O + K_2CO_3 + 3KCl + 3H_2O.$$
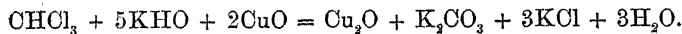
Chloroform vapour passed through a red-hot tube along with hydrogen liberates HCl. The operation may be performed in an apparatus like Marsh's for AsH_3, the flask being warmed.

Alcoholic KHO or NaHO, warmed with a chloroform solution to which a few drops of aniline have been added, gives benzoisonitrile, C_6H_5NC, a liquid of most penetrating and disagreeable odour.

27

ACETONE, $\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{CO}}$, dimethylketone, is a colourless liquid, obtained on a large scale by the distillation of calcium, barium, strontium, or magnesium acetates. It is contained in very small amount in blood, urine, &c., especially in cases of fever and diabetes. Many organic substances on dry distillation yield acetone amongst other products. It boils at 56·5°. Specific gravity, ·8179 at 0°. It mixes with water, alcohol, ether, chloroform, in almost any proportion. $CaCl_2$ separates it from water. Dehydrating substances act readily on acetone, forming mesitylene oxide, $C_6H_{10}O$, and phorone, $C_9H_{14}O$. H_2SO_4 will form also trimethyl benzene.

With NH_4HO and iodine iodoform is produced. Alcohol does not give iodoform with ammonia. Acetone in the presence of KHO dissolves HgO. $HgCl_2$ solution is made strongly alkaline with KHO, and then shaken with the supposed acetone solution and filtered. The filtrate will contain Hg if acetone was present. The compound formed is $2(C_3H_6O)3HgO$. A saturated solution of $HNaSO_3$ forms $C_3H_6ONaHSO_3$ with a solution of acetone. It is less soluble in alcohol than water. This is a method of purification of acetone.

Acetone is much used as a solvent for gun-cotton and other nitrated celluloses, in the manufacture of smokeless powders, and for other purposes.

ETHYL ACETATE, acetic ether or ester, $CH_3COOC_2H_5$, is a typical ester. It results from the action of acetic acid on alcohol. $C_2H_5OH + CH_3COOH = H_2O + C_2H_5OOCCH_3$. The simplest mode of formation is to distil a mixture of alcohol and acetic acid (molecular proportions of each) with about half a molecular proportion of concentrated sulphuric acid. The H_2SO_4 retains the water, and the ester distils over at about 70–80° C. Pure ethyl acetate boils at 72·5° C. Relative weight = ·91. It dissolves in about twelve parts of water, and also dissolves water.

It has a pleasant, characteristic odour. (Most esters are volatile, and the odours of their vapours, if not alike, are related.) It is decomposed by alkali hydroxides, alcohol being liberated, and by ammonia, with production of acetamide, CH_3CONH_2.

GLYCERINE (glycerol), $CH_2(OH).CH(OH)CH_2(OH)$, is a trihydric alcohol obtained as a by-product from vegetable oils and animal fats mainly in the processes of making soap and candles.

Glycerine is a colourless and odourless syrupy liquid. It has a sweet taste; dissolves in water, alcohol, and many other liquids in almost any proportion; absorbs water from the air up to nearly 50 per cent. of its weight. It does not vaporise until heated to much above 200° C., so that it may be dehydrated by heating. It can be obtained in crystals, but with difficulty. The crystals are said to melt at 22° C.; they are very deliquescent.

The relative weight of pure glycerine at 15° C. = 1·26 (water at 4°). The boiling-point = 290° C. under 760 mm.

Glycerine is an excellent solvent for many salts, oxides, &c., and many organic compounds. The alkali metals and ammonia combine with it, displacing the hydroxylic hydrogen. Acids can form three kinds of esters, such as the mono-, di-, and tri-acetate, and the corresponding nitrates. Nitro-glycerine is the trinitrate, $CH_2(NO_3)CH(NO_3)CH_2(NO_3)$.

Glycerine decomposes when distilled under ordinary pressure, or boiled for some time, giving off water and forming diglycerol, $C_6H_{14}O_5$, &c. It must therefore be purified by distillation with superheated steam.

CELLULOSE, $(C_6H_{10}O_5)_n$,* occurs in an approximately pure state in cotton, flax, and wood-fibre generally. It occurs in most plant tissues, and may be considered as the skeleton or basis of the vegetable kingdom. Manufactured cotton, linen, paper, &c., represent more or less impure conditions of this substance.

Although its chemical composition is very close or perhaps identical with that of the starches and some other carbohydrates, it is well distinguished by its insolubility in water and most other reagents. Its microscopic structure varies with the source, but its chemical character is quite definite. To isolate cellulose from almost any vegetable matters (cotton-wool or filter paper), treat with cold bromine water for fifteen minutes and then boil in dilute ammonium hydroxide. Repeat this treatment until the material has become quite white and the ammonia solution ceases to dissolve anything more.

It is doubtful if there be any simple solvent for cellulose in the sense that water is for sugar.

Concentrated acids, as H_2SO_4, HNO_3, and acetic, dissolve it slightly, under certain conditions of temperature, forming salts with it. A triacetate of cellulose is well known, and gun-cotton is probably a trinitrate. The ordinary gun-cottons or collodion cottons are mostly, however, complex mixtures of nitrates.

With powerful bases, as $Ba(HO)_2$ and KHO, it seems to form salts, acting in these cases as the negative or acid radical towards the strong base.

Unlike starch, cellulose is not turned blue by iodine, but any cellulose substance moistened with a solution made by dissolving equal weights of zinc chloride and potassium iodide in strong HCl (Schultz's reagent), and then washing the brown stain with water, becomes blue or purple.

Cupramine, $Cu\genfrac{}{}{0pt}{}{NH_2}{NH_2}$, made by dissolving copper oxide in strong ammonia solution, dissolves cellulose to a thick, gummy solution. The fibres are observed first to swell considerably before dissolving.

This solution, when diluted very largely with water or an acid, deposits cellulose in a gelatinous form.

* Jute, cork, the mass of which apples, turnips, &c., consists, are probably modifications from cellulose or oxycelluloses. A good deal of work is still required at these compounds to elucidate some clear idea of their constitution.

STARCH ($C_6H_{10}O_5$).*—May be considered as an isomeride of cellulose. It occurs in nearly all parts of plants. It is most abundant in the grain of cereals, and in tubers like the potato. In all cases it exists in cells, which vary in size and shape, depending on the plant.

Starch is insoluble in cold water, and is separated from grain or potatoes by trituration and washing by a stream of water. The cells are carried away from the cellular tissue, &c., and fall as a white powder on allowing the water to stand for some time.

The grains or cells of starch from any one source are moderately regular in shape ; those from cereals are smaller than from tubers.

On heating in a closed tube starch decomposes in a similar manner to woody fibre, giving off water and combustible gases, and leaving charcoal.

Shake up some starch with cold water in a test-tube ; it does not dissolve, and will settle to the bottom unchanged on standing. Add twice its volume of boiling water, and shake. The mass forms a semi-transparent jelly. On heating to boiling, or nearly so, apparently complete solution takes place. Add an alcoholic solution of iodine or a solution of iodine in potassium iodide to a starch emulsion ; a fine blue colour—iodide of starch—is produced. The colour varies from purple to blue. It is destroyed on heating, but reappears on cooling. (See tests for nitrites.)

A starch solution, when heated for some time with a little acid, HCl or H_2SO_4, or with partially germinated grain solution, undergoes several changes.

DEXTRINE.—Dilute a few c.c. of a starch solution made as above, add a few drops of HCl or H_2SO_4, dilute, and heat to nearly boiling. Pour out a few drops from time to time into an iodine solution, until only a brown coloration is produced. At this point the starch has been converted into an isomeride, termed dextrine, which may be precipitated in a flocculent state by adding alcohol to the acid solution.

GLUCOSE (dextrose or grape-sugar).—A dilute solution of starch when boiled with the addition of a few drops of HCl or H_2SO_4, until no further reaction is given with iodine, becomes converted into glucose.

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6.$$
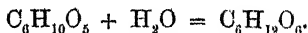
Grape-sugar is contained in many plants or fruits—from grapes, which contain about 14 per cent., to peaches, with little more than 1 —in honey along with lævulose, and in diabetic urine. Dextrose crystallises from water as $C_6H_{12}O_6.OH_2$. It dissolves in $1\frac{1}{3}$ its own weight of water.

All glucoses, when warmed with an alkaline copper tartrate solution, cause a yellow or red precipitate of Cu_2O. Cane-sugar, dextrine, gum arabic, glycerine, urea, and a number of organic acids

* See Cross and Bevan (*Chem. Soc. Journ.* and separate publications).

do not reduce the copper solution in this manner, or only after long boiling.

Glucose, $C_6H_{12}O_6$ reduces 10, lactose, $C_{12}H_{22}O_{11}$ 7, and maltose, $C_{12}H_{22}O_{11}$, 6 molecules of CuO to Cu_2O.

Glucoses may be fermented. Add a small quantity of yeast to a test-tube of dilute dextrose or grape-sugar, fit with cork and delivery tube; keep in a warm place—about 25° C.; in about an hour gas, CO_2, will be evolved. Collect and test with lime- or baryta-water. On boiling after evolution of gas has nearly ceased, alcohol comes off, and may be distinguished by its odour; or it can be oxidised to acetic acid by permanganate and tested for. A molecule of glucose yields on fermentation two molecules of carbon dioxide and two of alcohol; .

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2.$$

BENZENE, C_6H_6. Specific gravity, 0·85 at 15·5°. Boiling-point, 80·4° at 760 mm.—Is a liquid which, when cooled below 0° C., sodidifies into fern-like tufts, melting again at 5·5° C. It is a non-conductor of electricity. At the ordinary temperature it is a limpid, colourless, strongly refracting liquid, having a pleasant odour; slightly soluble in water; readily miscible with ether, wood spirit, and acetone. It dissolves sulphur, phosphorus, and iodine, especially on heating, fixed and volatile oils, camphor, wax, caoutchouc, &c.

Benzene has a low flash-point, and its vapour burns with a bright, smoky flame. When its vapour is passed through a red-hot tube carbon is separated, and gaseous and solid hydrocarbons (diphenyl principally) are formed. Chlorine and bromine act upon it in sunshine, forming both addition and substitution products. It is not acted upon by alkalies, but potassium acts upon it, forming a blue-coloured compound, which is explosive, or explodes on contact with water. Strong nitric acid converts it into nitrobenzene,

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O.$$
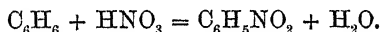
Nitrobenzene is a nearly colourless liquid at ordinary temperatures, which boils at 206° C. It has an odour something like that of bitter almonds. Water scarcely dissolves it, but it is soluble in alcohol, ether, and many other liquids, and very volatile in steam. Sulphuric anhydride or fuming sulphuric acid forms with benzene sulphone $(C_6H_5)_2SO_2$, and strong sulphuric acid $C_6H_5HSO_3$, phenyl sulphonic acid on long heating.

Detection of Benzene.—The liquid to be tested is warmed in a test-tube with strong nitric acid, then diluted with water, and shaken up with ether, which dissolves the nitrobenzene.

The ethereal solution is mixed with a little alcohol and strong HCl, and a few pieces of zinc added. After about five minutes' rapid evolution of hydrogen from the zinc the solution is poured off, excess of KHO added, and then if the aniline formed be in too small quantity to separate, ether is added, and the ethereal solution separated and evaporated on a watch-glass. On adding a few drops of chloride .

of lime solution to the oily residue on the watch-glass a purple colour is formed if aniline be present, which thus indirectly indicates benzene.

The action of nascent hydrogen on nitrobenzene may be represented thus :

$$C_6H_5NO_2 + 3H_2 = 2H_2O + C_6H_5NH_2.$$
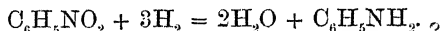
ANILINE is a colourless liquid boiling at 193° C. Aniline easily oxidises and becomes then yellowish or brown. It is scarcely soluble in water, but dissolves in alcohol and ether and some other oily liquids. With all acids it forms salts, such as $C_6H_5NH_2HCl$, which crystallise well and are all soluble in water. It is a most characteristic "amine" base, and behaves very much like ammonia. Nitrous acid acts upon it so as to produce diazobenzene or phenol, according to conditions of temperature and amount of water present.

$$C_6H_5NH_2HCl + HNO_2 = C_6H_5NNCl + 2H_2O, \text{ and}$$
$$\text{Diazobenzene chloride.}$$

$$C_6H_5NNCl + H_2O = C_6H_5OH + HCl + N_2.$$
$$\text{Phenol.}$$
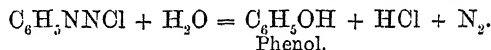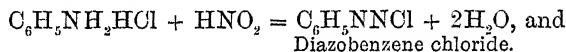
This constitutes the "diazo" reaction.

PHENOL, $C_6H_5.OH$ (carbolic acid), is the hydrate or hydroxide of benzene. It occurs in castor oil, and in the urine of some herbivorous animals, but the practical source is coal-tar oils.

When pure, phenol consists of large colourless prisms, which have a peculiar odour and produce a burning taste. It melts at 42°, and boils without decomposition at 181·5°. When not quite pure it is slightly coloured red or brown. Phenol is soluble in fifteen parts of cold water, but much more readily in alcohol. Its solution is a powerful antiseptic and caustic, and it is also highly poisonous.

Bromine water added to a phenol solution forms tribromophenol, a yellow solid, which is somewhat insoluble, 1 part in 60,000 of water, and therefore precipitates. Concentrated nitric acid converts phenol into trinitrophenol or picric acid. The action may become very violent even with quantities of a few grams. Dilute nitric acid will form a mixture of mono-nitrophenols. Picric acid is made by the action of hot dilute nitric acid on the phenol-sulphonic acid, $C_6H_4OHSO_3H$ (1 : 4) obtained by heating equivalent quantities of phenol and sulphuric acid to 120°-150° C.

$$C_6H_4OHSO_3H + 3HNO_3 = C_6H_2.OH.(NO_2)_3 + 2H_2O + H_2SO_4.$$
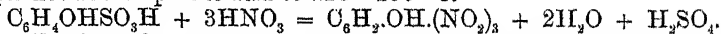
Picric acid unites with alkalies and metallic oxides generally the picrates formed being in all cases explosive when dry. The acid is soluble in alcohol; this solution dyes silk or wool yellow. On adding ammonium hydroxide to a phenol solution, and then a hypochlorite or hypobromite, a fine blue colour is produced.

The phenols are all acidic compounds, and combine with metals, or metallic hydroxides, giving salts, as C_6H_5OK, commonly called potassium phenylate.

Ferric chloride, added to a solution of phenol in water, produces a fine purple colour (1 part in 3000 water). Albumen solution is coagulated on addition of phenol. Phenol boiled with Millon's reagent (mercuric nitrate with excess of nitric acid) produces a fine red colour, permanent for some time.

CARBON DISULPHIDE, CS_2. Specific gravity, 1·263. Boiling-point, 46·6 C°. Refractive power, 1·645.—Disulphide of carbon is a colourless, very mobile, highly refracting liquid, having a peculiarly unpleasant odour. It evaporates quickly at ordinary temperatures, producing great cold. It is almost insoluble in water, but alcohol and ether mix with it in all proportions. It dissolves sulphur, phosphorus, iodine, caoutchouc, oils, and fat, for which purposes it is largely used.

Disulphide of carbon vapour is very inflammable, and burns with a blue flame, producing sulphur and carbon dioxides. A mixture of its vapour and nitric oxide burns with a very bright blue flame, particularly rich in chemically active rays.

Dry chlorine converts it in the presence of iodine into tetrachloride of carbon and sulphochloride of carbon, $CSCl_2$. The alkali oxides gradually dissolve disulphide of carbon, forming a brown solution which is a mixture of carbonate and sulphocarbonate of the alkali metal:

$$3CS_2 + 3K_2O = K_2CO_3 + 2K_2CS_3.$$
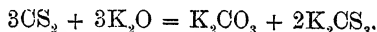
An aqueous or alcoholic solution of potassium hydroxide to which a little lead salt—acetate—has been added, boiled with disulphide of carbon, becomes blackened. This is a very delicate test for sulphide of carbon.

With triethylphosphine it unites directly, forming a compound, $P(C_2H_5)_3CS_2$, which crystallises in splendid ruby-coloured prisms, which dissolve in ether with a red colour. This is a good test for CS_2 vapour in other gases.

UREA, $CO{NH_2 \atop NH_2}$.—Is the chief form in which the waste nitrogen of the body escapes in the urine. It was synthesised by Wöhler from ammonium cyanate, NH_4OCN, which undergoes a molecular change on the evaporation of its solution. It was previously made by J. Davey, but not fully recognised.

Urea forms colourless crystals, which deliquesce in moist air; they are easily soluble in water and alcohol, but scarcely in ether. It melts at 130° C., and it then begins to decompose into cyanuric acid and biuret.

Heat a little urea in a test-tube until ammonia is evolved, add warm water; biuret dissolves, and on adding a little $CuSO_4$ solution, and then excess of NaHO, a violet colour is produced.

Oxalic acid added to a solution of urea gives a crystalline precipitate of the oxalate, rapidly from strong, after some time from dilute, solutions.

Nitric acid, quite free from lower oxides of N, forms urea nitrate, which is also crystalline and soluble in water; very slightly so in nitric acid.

Mercuric nitrate precipitates from urea solutions, when the latter is in excess, white $(CON_2H_4)_2(HgO)_3$.

This precipitate is sometimes employed in the estimation of urea quantitatively.

Urea heated with KHO gives ammonium carbonate and then NH_3.

Nitrous acid, or an acid solution of a nitrite, decomposes urea, liberating N and CO_2.

$$CON_2H_4 + 2HNO_2 = 2N_2 + CO_2 + 3OH_2.$$
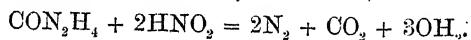
Alkali hypobromite or hypochlorite causes immediate effervescence, all the nitrogen being liberated.

$$CON_2H_4 + 3NaOBr + 2NaHO = N_2 + 3NaBr + 3OH_2 + Na_2CO_3.$$
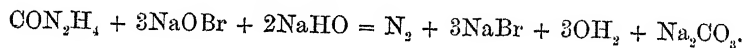
SEPARATION OF ALCOHOL, ALDEHYDE, ACETONE, ETHER, PARAFFIN HYDROCARBONS, BENZENE, CHLOROFORM, GLYCERIN, CARBON BISULPHIDE, PHENOL, NITROBENZENE, ANILINE, ESTERS, FROM A MIXTURE.

1, Much information may be obtained from odour,

2, Test for acid or alkaline reaction,

If acid—Free organic acids, phenols.

If alkaline—Amines, as aniline.

3, Add to the solution increasing amounts of water, and note whether—

(a) The liquid in part or wholly dissolves,

Alcohol, aldehyde, acetone, glycerine, phenol, and a few esters dissolve fairly easily.

Note.—The presence of one organic liquid soluble in water may cause considerable quantities of an otherwise insoluble one to dissolve.

(b) There is an insoluble portion : 1. Heavier than water. Nitrobenzene, aniline, carbon disulphide, chloroform.

2. Lighter than water. Paraffin hydrocarbons, benzene, ether, certain esters.

4. If no separation with water, distil a portion of original. If a separation can be effected, distil a portion of both the soluble and insoluble parts, collecting in any case a few c.c., noting temperature of distillation and odour of distillate. Glycerine can always be removed by water, and generally recovered by evaporation and heating to above 100° C.

(a) Readily volatile—Alcohol, aldehyde, ether, paraffin hydrocarbons, benzene, carbon disulphide, chloroform, some esters.

Addition of potassium carbonate, if but little water is present, will cause alcohol to separate.

Addition of a saturated solution of sodium bisulphite will separate aldehyde and acetone as crystalline compounds.

Special tests may be applied to the distillate (or original liquid if little or no water appears present).

1. *Iodoform reaction.*—Add a few drops iodine solution in KI, then sodium hydroxide solution until colour disappears. Warm and set aside. Yellow crystals of iodoform, easily recognised by odour, separate—*ethyl alcohol, acetone, aldehyde* (and some other compounds containing a CH$_3$ group).

2. *Reduction of AgNO$_3$.*—Add NH$_4$HO to silver nitrate till the precipitate first formed just disappears. Add a few drops of liquid to be tested, and stand tube in beaker of boiling water. Silver mirror—*aldehydes.*

3. *Schiff's reaction.*—Just decolorise magenta* solution by adding sulphurous acid. Add a few drops of liquid. Colour is restored—*aldehyde.*

4. *Carbamine reaction.*—Warm a few drops with one drop of aniline and a few drops of alcoholic potash. Unpleasant odour of phenyl carbamine—*chloroform.*

5. Nitrobenzene will always be evident from its characteristic odour. If absent, then a little of the liquid may be treated with a few drops of strong HNO$_3$, warmed. Nitrobenzene odour—*benzene.*

(b) Portion not volatile below 100° C. may contain glycerine, phenol, nitrobenzene, aniline, certain esters, &c,

Test with litmus : *If acid,* free organic acids may be present, or phenol.

Shake up with dilute KOH, which will remove acid substances.

If alkaline, possibly amines or aniline are present. Shake up with dilute HCl to remove them.

* Magenta is an aniline colour.

APPENDIX III.

ALKALOIDS form a class of organic compounds which act as bases combining with acids to form salts. Most alkaloids are of vegetable origin and contain nitrogen and oxygen, exceptions to the latter being found in the liquid volatile alkaloids, conine and nicotine. The exact constitution of many of them is uncertain, but a considerable number have been synthetically prepared, and they all appear to be derivatives of pyridine (C_5H_5N).

The alkaloids generally have an alkaline reaction, and can neutralise acids, forming well-defined salts. The alkaloids are generally almost insoluble in water (the liquid ones, conine and nicotine, forming exceptions), but soluble in alcohol, ether, chloroform, and other organic solvents.

The salts are more soluble in water than the alkaloids themselves, but in many cases combination with the base is so feeble that water breaks them up, setting free the alkaloid. Stronger inorganic bases (KOH, Na_2CO_3) always sets free the alkaloid.

The solutions of alkaloids exhibit optical activity—that is, they are capable of causing rotation in a beam of polarised light, generally in a lævo-rotatory direction.

The reactions of the more common alkaloids, conine, nicotine, morphine, narcotine, quinine, cinchonine, strychnine, brucine, atropine, and cocaine are here given.

If the alkaloids to be tested are mixed with various foreign organic matters, they must first be separated by means of precipitation by various general reagents. The reagents which either precipitate all the alkaloids or most of them are: (I.) $PtCl_4$; (II.) a solution of iodine in KI; (III.) potassio-mercuric iodide; (IV.) potassio-cadmium iodide; (V.) potassio-bismuthous iodide; (VI.) phosphomolybdic acid; (VII.) phosphoantimonic acid; (VIII.) phosphotungstic acid; and (IX.) picric acid.

By means of these reagents the alkaloids are precipitated in various states, and suitable methods must then be used to separate the alkaloids from the compounds formed, which will readily be suggested from the reactions of the various precipitants of the above reagents. KHO or $NaHCO_3$ will, for example, decompose most of the above compounds, setting free the alkaloid, which may be

obtained by extraction with a suitable solvent immiscible with water such as (chloroform, &c.).

Should no precipitate be obtained with a solution of iodine in KI, this may be regarded as a positive proof of the absence of alkaloids, but a precipitate may be given by substances other than alkaloids.

Both platinic and auric chlorides unite with alkaloids, or rather with their hydrochlorides, forming double salts, very similar to the manner in which ammonium chloride and chlorides of bases of the aniline type, as $C_6H_5NH_2HCl$, unite with these chlorides.

Most of these combinations can be decomposed by SH_2.

Picric acid combinations are generally easily decomposed by ammonia.

Many of the crystalline precipitates obtainable with the alkaloids may be well observed by carrying out the test on a watch-glass or microscope slide, under a low power (one inch) with the microscope.

Colour Tests.—Having ascertained that an alkaloid is present, its identification largely depends on certain colour reactions with acids and other reagents. To carry out such tests a little of the separated base (or salt) should be treated with a drop of the reagent in a white porcelain dish.

Two special reagents—Frohde's and Erdmann's are prepared respectively as follows :

Frohde's reagent.—·005 grm. of sodium (or ammonium) molybdate dissolved in 1 c.c. of concentrated H_2SO_4.

Erdmann's reagent.—Six drops of HNO_3 mixed with 100 c.c. of water, and ten drops of this solution added to 20 grms. of pure concentrated H_2SO_4.

A summary of the principal colour reactions will be found later.

MORPHINE.

The alkaloids may be divided into two groups, volatile and non-volatile. To the first group belong only nicotine and conine amongst those most frequently occurring. The second group may be divided into three sub-groups: I. Alkaloids precipitated from solutions of their salts by KHO or NaHO, but soluble in excess of the precipitant. II. Alkaloids precipitated by KHO or NaHO, but insoluble in excess. They differ from the alkaloids of the third sub-group in being thrown down from acid solutions by $NaHCO_3$. III. Alkaloids precipitated by KHO or NaHO, insoluble in excess, but not precipitated from acid solutions by $NaHCO_3$.

I. ALKALOIDS PRECIPITATED BY KHO, SOLUBLE IN EXCESS.

MORPHINE (OR MORPHIA), $C_{17}H_{19}NO_3$.

Morphine occurs, together with narcotine and several other less important alkaloids, in opium, the dried milky juice of the green

capsules of the poppy (*Papaver somniferum*). Morphine crystallises with one molecule of water, and usually forms either brilliant white needles, rhombic prisms, or a crystalline powder. It has a bitter taste, is almost insoluble in water, and but slightly so in alcohol and ether. Its best solvent is amyl alcohol. Morphine parts with its water of crystallisation at $100°$, and if carefully heated may be sublimed without decomposition.

A solution of morphine hydrochloride (hydrochlorate) of about 1 per cent. is employed for the reactions.

NH_4OH precipitates after some time a white precipitate of $C_{17}H_{19}NO_3,OH_2$. The precipitate is readily soluble in $NaHO$ and KHO, but with more difficulty in ammonium hydroxide. It is also soluble in NH_4Cl, and with difficulty in $(NH_4)_2CO_3$.

Acid and normal alkali carbonates give the same precipitate, insoluble in excess.

Concentrated HNO_3 gives with solid morphine or one of its salts a yellowish red colour, not altered to violet by $SnCl_2$ or thiosulphate. (Distinction from brucine.)

Cold concentrated H_2SO_4 dissolves morphine to a colourless solution. If this solution is allowed to stand for twelve hours, and then heated to $150°$ for a short time, and after cooling a drop of HNO_3 of density $1·2$ added on a porcelain plate, a coloration is observed, which is sometimes violet at first, changing to blood-red and then yellow.

A crystal of potassium bichromate added to the H_2SO_4 solution gives a green colour, whereas MnO_2 gives no coloration. (Distinction from strychnine.)

Frohde's reagent, or a molybdate of an alkali in strong H_2SO_4, added to morphine or a dry salt of morphine, gives a deep violet colour at once; this colour gradually changes to olive-green, and then to a deep blue on stirring.

If a small quantity of morphine be dissolved in about 1 c.c. of concentrated HCl, a drop of strong H_2SO_4 added, and the mixture heated on the water-bath until the HCl is driven off, a purplish residue is obtained. This residue is treated with a little HCl, and neutralised with a cold saturated-solution of $HNaCO_3$, and then one drop of an alcoholic solution of iodine added—the liquid becomes emerald-green. On shaking with ether the substance (apomorphine) is dissolved to a violet-red solution.

Fe_2Cl_6 (neutral) or solution of iron alum gives, with strong solutions of morphine salts, a dark-blue coloration, changed to green by excess and destroyed by the addition of acids; large excess of ferric chloride should be avoided.

On adding a fresh solution of potassium ferricyanide with Fe_2Cl_6 a blue colour is produced owing to reduction of the ferric salt. (Distinction from cinchona bases; compare cocaine.)

II. Non-volatile Alkaloids, Precipitated by KHO or NaHO, Insoluble in Excess, also Precipitated by $HNaCO_3$, even from Acid Solutions.

NARCOTINE, $C_{22}H_{23}NO_7$.

Narcotine is found together with morphine in opium. It is insoluble in water, and only sparingly soluble in alcohol, ether, and light petroleum. It is easily soluble in benzene, but its best solvent is chloroform. Narcotine melts at 170°. All narcotine salts possess an acid reaction.

Any salt of narcotine may be employed for the reactions.

All alkalies, their carbonates and bicarbonates, precipitate narcotine immediately in the form of a white powder, crystalline as seen under the microscope.

Concentrated HNO_3 dissolves narcotine on warming, with evolution of nitrous fumes, and forms a reddish yellow solution; on heating more strongly more fumes are given off, and the solution becomes yellow.

Concentrated H_2SO_4 dissolves narcotine with a pale greenish yellow colour, changing to pure yellow. On heating in a porcelain dish, the solution becomes orange-red and violet-blue at the edge, and when the sulphuric acid begins to evaporate it assumes a dirty reddish violet colour.

If a small quantity of narcotine be dissolved in Erdmann's reagent, a brownish colour is first formed, becoming red.

Frohde's reagent dissolves narcotine, forming a green solution. If the solution, however, contains double the amount of sodium molybdate, the green colour changes to a magnificent cherry-red.

Chlorine water gives a yellow colour, changed by NH_4OH to a yellowish red or orange.

If a solution of narcotine in strong H_2SO_4 is heated until the red coloration appears, and then Fe_2Cl_6 added, the portions of the liquid in contact with the ferric chloride become red, with brilliant violet edges, and after ten or fifteen minutes a cherry-red coloration is produced.

If narcotine or one of its salts be dissolved in dilute H_2SO_4 and MnO_2 added, and the mixture boiled, the alkaloid is oxidised into opianic acid, cotarnine, and CO_2. On filtering and adding NH_4OH, no precipitate is produced.

QUININE, $C_{20}H_{24}N_2O_2$.

Quinine occurs in cinchona barks, together with cinchonine and several other bases. It may be obtained crystallised either anhydrous or with three molecules of water of crystallisation. In the hydrated state it effloresces on exposure to the air. Quinine is

sparingly soluble in cold, but more readily soluble in hot water, but still more so in alcohol, ether (distinction from cinchonine), chloroform, and carbon disulphide. Crystallised quinine melts at 57° in its water of crystallisation, which it loses at 100°; when anhydrous it melts at 177°.

The neutral salts of quinine are sparingly soluble in water; the acid salts, however, are readily soluble, and solutions of many of them, especially the sulphate, exhibit a bluish fluorescence. A solution of quinine sulphate acidulated with dilute H_2SO_4 turns the polarised ray strongly to the left. (Distinction from cinchonine.)

The alkalies and their normal carbonates precipitate quinine from not too dilute solutions in the form of an amorphous powder, which soon becomes crystalline, as seen under the microscope. If a salt of quinine be precipitated by means of ammonium hydroxide, ether (containing 2 per cent. of alcohol) added, and the mixture shaken, the precipitated quinine redissolves in the ether, and the clear liquid forms two layers. Quinine may be separated from cinchonine by this process.

$HNaCO_3$ forms a precipitate only from moderately strong solutions; the precipitate is somewhat soluble in excess, and contains carbonic acid.

Strong HNO_3 dissolves quinine to a colourless solution, becoming yellowish on heating. A nitro derivative is formed.

Concentrated H_2SO_4 dissolves quinine and its salts, forming a colourless or faintly yellow solution; on heating the colour changes to yellow, and afterwards to brown.

Erdmann's reagent only gives a faint yellow colour.

Chlorine or bromine water (about one-fifth its volume) added to a solution of a quinine salt does not colour the solution, but on the addition of NH_4OH in excess an intense emerald-green colour is produced (distinction from cinchonine). If after the addition of chlorine water some solution of K_4FeCy_6 is added, and then a few drops of NH_4OH, the solution acquires a deep red tint, speedily changing to a dirty brown. The red colour is destroyed by an acid, but may be reproduced by the cautious addition of NH_4OH. This reaction is most characteristic, but is interfered with by the presence of morphine.

If quinine sulphate is dissolved in a little acetic acid, alcohol added, and then sufficient alcoholic solution of iodine to colour the liquid brownish, the sulphate of iodoquinine (herapathite) separates out after a short time as a black crystalline powder, or in the form of plates, which are beautifully dichroic, and polarise light strongly. This reaction is very characteristic, and, by the employment of the microscope, very delicate.

CINCHONINE, $C_{19}H_{22}N_2O$.

Cinchonine occurs in cinchona bark, together with quinine and other alkaloids. It forms either transparent, brilliant rhombic prisms

or fine white needles, or, if precipitated from concentrated solutions, a loose white powder.

Cinchonine is almost insoluble in both hot and cold water. It is but sparingly soluble in cold alcohol, but somewhat soluble on boiling, from which solution most of the cinchonine crystallises on cooling. It is almost insoluble in ether (distinction from quinine), chloroform, and light petroleum, but dissolves readily in chloroform mixed with one-fourth or one-third of its bulk of alcohol.

When cinchonine is cautiously heated it melts at 165° and gives off white fumes, which condense upon cold surfaces in the form of small brilliant needles, or as a loose sublimate, a peculiar aromatic odour being exhaled at the same time.

Cinchonine salts are in general more soluble than the corresponding quinine compounds. The solutions are not fluorescent, and turn the polarised ray to the right.

Alkalies and their normal carbonates immediately precipitate amorphous cinchonine, insoluble in excess.

$HKCO_3$ and $HNaCO_3$ give the same precipitate.

Concentrated H_2SO_4 dissolves cinchonine, forming a colourless liquid, which on warming becomes first brown, and finally black; the same change of colour is noticed on the addition of HNO_3.

Frohde's reagent gives no coloration.

Erdmann's reagent gives no coloration.

Chlorine water causes no changes of colour, but on adding NH_4OH a yellowish white precipitate is produced.

If K_4FeCy_6 is added to a neutral solution of a cinchonine salt, a yellowish flocculent precipitate of cinchonine ferrocyanide is formed. On the addition of excess of the precipitant, and on gently and slowly heating, the precipitate dissolves, but separates on cooling in brilliant gold-yellow scales, or in long needles, often aggregated in the shape of a fan. With the aid of a microscope this reaction is most delicate and characteristic.

Quinine and cinchonine may be separated from narcotine by repeatedly shaking up the acidified solution with chloroform; the chloroform is then separated, and ammonia and ether containing 2 per cent. of alcohol added to the aqueous solution, when the cinchonine separates out, and the quinine dissolves in the ether. The alkaloids may then be readily tested by the reactions given above.

III. Non-Volatile Alkaloids, Precipitated by KHO or NaHO, Insoluble in Excess; not Precipitated by $HNaCO_3$.

STRYCHNINE, $C_{21}N_{22}N_2O_2$.

Strychnine is found, together with brucine, in the fruit of the *Strychnos nux-vomica* and *Strychnos ignatii*. It occurs either in white, brilliant, rhombic prisms, or as a white powder. It possesses

an alkaline reaction, and is intensely bitter. Strychnine is almost insoluble in water, absolute alcohol, ether, and light petroleum. It is slightly soluble in ether containing water and alcohol, amyl alcohol and benzene, but very readily soluble in chloroform.

Strychnine does not melt without decomposition, but by careful heating small quantities may be sublimed unchanged.

Most salts of strychnine are soluble in water and alcohol, insoluble in ether, chloroform, amyl alcohol and benzene. All the salts taste intensely bitter, and are very poisonous.

KHO, $NaHO$, and Na_2CO_3 precipitate strychnine as a white crystalline powder, insoluble in excess.

NH_4OH gives the same precipitate, soluble in excess; after a short time, however, the strychnine crystallises from its solution in the ammonium hydroxide in the form of needles. $HNaCO_3$ added to a neutral solution of a strychnine salt precipitates the alkaloid in the form of fine needles, insoluble in excess. If, however, a drop of acid be added, so as to form free carbonic acid, the precipitate is redissolved, although the solution may still be alkaline. As the liberated carbon dioxide escapes on exposure to the air, the strychnine is gradually reprecipitated.

Strong H_2SO_4, strong HNO_3, Frohde's reagent and Erdmann's reagent, all fail to give colorations with strychnine.

If strychnine is dissolved in concentrated H_2SO_4, and then brought into contact with any oxidising agent (such as K_2CrO_4, $K_2Mn_2O_8$, $K_6Fe_2Cy_{12}$, PbO_2, or MnO_2), best in the solid condition, the liquid assumes a magnificent blue-violet colour, which changes to red and then to reddish yellow. The reaction may be performed by precipitating the strychnine as a chromate by means of K_2CrO_4, freeing the precipitate from moisture as far as possible, and treating it on a watch-glass with strong H_2SO_4, when the blue-violet or blue colour is observed.

Curarine gives the same reaction as strychnine, but is coloured red by strong H_2SO_4 alone.

The most delicate reagent for strychnine is the green liquid obtained by dissolving 1 part of $K_2Mn_2O_8$ in 2000 parts of strong H_2SO_4, and adding to the strychnine solution, but under these conditions other organic substances may cause a similar colour to be generated. This reaction is impaired by the presence of chlorides, nitrates, and large quantities of organic matter, from which the strychnine should be obtained as free as possible.

If a few drops of a solution of ammonium vanadate in 100 to 200 parts of strong H_2SO_4 be added to a little strychnine on a watch-glass and allowed to remain a few moments until the mixture becomes darker in colour, and the watch-glass then slightly inclined, a magnificent blue colour will be seen at the moment the vanadium sulphate solution runs off the residue; this colour soon turns to violet, and then to vermilion or reddish yellow. If KHO or $NaHO$ be added as soon as the red colour appears permanent a rose or purplish red colour is produced, which becomes more brilliant on dilution. This reaction is not so delicate as the previous

one, but has the advantage of scarcely being affected by other organic matter.

A little of the alkaloid dissolved in fuming HNO_3, the acid evaporated off on a water-bath, and the residue just touched with a solution of alcoholic KHO, gives a red coloration (compare atropine and brucine).

Chlorine water gives a white precipitate, soluble in ammonium hydroxide to a colourless liquid.

KSCN gives immediately from strong solutions, but only after some time from dilute solutions, a white crystalline precipitate, insoluble in excess.

$HgCl_2$ forms a white precipitate consisting of clusters of needles; it is soluble on boiling, but recrystallises on cooling.

Potassium ferrocyanide throws down a white or yellowish white precipitate—a reaction which may be utilised for separating strychnine from brucine.

BRUCINE, $C_{23}H_{26}N_2O_4$.

Brucine occurs together with strychnine in different kinds of strychnos.

It crystallises with four molecules of water in the form either of right rhombic prisms, clusters of needles, or a white crystalline powder.

Brucine is sparingly soluble in cold, but rather more so in hot water. It is readily soluble in alcohol, amyl alcohol, and chloroform, but less so in benzene, and almost insoluble in absolute ether. It possesses an intensely bitter taste.

When heated, brucine fuses with loss of its water of crystallisation, but on careful heating it may be sublimed unchanged. Its solution in alcohol rotates the polarised ray to the right.

KHO, NaHO, and Na_2CO_3 precipitate brucine, insoluble in excess. The precipitate when first formed is granular, but may be seen under the microscope to change suddenly into needles, with the absorption of water.

NH_4OH produces a whitish precipitate with brucine salts; this precipitate appears to consist of minute oily drops, which gradually change with the absorption of water to small needles. The fresh precipitate, before absorption of water, is readily soluble in excess; but brucine soon crystallises from the solution in small groups of needles.

Strong HNO_3 dissolves brucine and its salts to an intensely red solution, which afterwards becomes a yellowish red, and yellow on warming. On the addition of $SnCl_2$, or colourless NH_4HS, to the solution, and then heating, an intense violet colour is formed; from concentrated solutions a violet precipitate. With $NaHS$ instead of the above reducing agents the violet colour afterwards changes to green.

Strong H_2SO_4 gives with brucine or one of its salts a pale rose colour, which afterwards becomes yellow.

Erdmann's reagent gives the same colours.

Frohde's reagent gives a red, changing to reddish orange, fading rapidly.

Treated with fuming HNO_3, evaporated, and the residue moistened with alcoholic potash, a greenish colour is produced (compare atropine and strychnine).

$Hg_2(NO_3)_2$, as free as possible from acid, gives a colourless solution which on heating on a water-bath gradually assumes a fine carmine colour. (Distinction from *strychnine*, which gives no colour with $Hg_2(NO_3)_2$.)

K_2CrO_4 gives a yellowish red crystalline precipitate after some time.

Chlorine water added to a brucine salt gives a bright red colour, changed by ammonium hydroxide to a yellowish brown.

KSCN gives a granular precipitate from strong solutions at once, from dilute solutions only after some time.

$HgCl_2$ gives a white granular precipitate.

Potassium ferrocyanide only slowly precipitates brucine from slightly acid solutions (compare strychnine).

ATROPINE, $C_{17}H_{23}NO_3$.

Atropine, or daturine, is an alkaloid, found in the deadly nightshade (*Atropa belladonna*) and in the thorn apple (*Datura stramonium*), from which the second name is derived. It forms crystalline needles, which melt at $114-115°$.

Atropine is somewhat soluble in cold water, more readily in hot. The solutions are rapidly turned yellow on exposure to air, and acquire a disagreeable odour. The solution reddens phenol phtalein, which is essentially different from the action of alkaloids derived from other families of plants. Atropine is very soluble in alcohol and chloroform, but not so soluble in ether.

The salts of atropine are soluble in water and alcohol, but hardly soluble in ether.

A solution of the sulphate may be employed for the tests.

NH_4HO produces a precipitate with salts of atropine, the precipitate being soluble in excess.

The alkalies and their normal carbonates precipitate atropine.

$NaHCO_3$ produces no precipitate.

HNO_3 (strong) produces no colour with atropine.

H_2SO_4 (strong) dissolves the salts without any coloration. On adding a drop of HNO_3 or a crystal of KNO_3 no colour is produced; but if a trace of potassium nitrite is added a deep yellow or orange colour is obtained, which is changed to a fine reddish violet on adding a little alcoholic solution of KOH.

HNO_3 (fuming) added to atropine, then the acid evaporated off,

and alcoholic solution of KOH added to the dry residue, a very characteristic violet colour appears, which changes to red (compare strychnine and brucine).

The free alkaloid (if a salt is under examination it may be decomposed by NH_4HO, and the base obtained by extraction with chloroform), when treated with a 2 per cent. solution of $HgCl_2$ in alcohol, produces a red coloration. All other common alkaloids produce either no precipitate or a white one.

$AuCl_3$ gives a yellow crystalline precipitate.

I in KI added to a solution acidulated with HCl throws down an amorphous precipitate of the tri-iodide, which is not dissolved by acetic acid.

COCAINE, $C_{17}H_{21}NO_4$.

Cocaine is the principal alkaloid found in coca (*Erythroxylon coca*) leaves, and is employed largely as a local anæsthetic. It is a crystalline substance, forming definite salts with acids. The alkaloid is only slightly soluble in water, but easily soluble in alcohol, ether, &c. The aqueous solution is strongly alkaline. The hydrochloride and hydrobromide are readily soluble in water and may be used for testing.

Alkalies and their carbonates precipitate cocaine.

NH_4HO also precipitates the alkaloid.

H_2SO_4 (strong) gives no colour with cocaine.

HNO_3—no coloration.

Erdmann's reagent (H_2SO_4 with HNO_3)—no coloration.

Frohde's reagent—no coloration.

Iodine in KI gives a rose-coloured precipitate from very dilute solutions of the hydrochloride.

$PtCl_4$ gives with strong solutions needle-shaped crystals of star-like form, but with more dilute solutions the crystals are prismatic.

$AuCl_3$ gives a precipitate in even the most dilute solutions.

These precipitates are definite compounds of the type of ammonio platinum salts, &c.

A mixture of freshly dissolved potassium ferricyanide and Fe_2Cl_6 gives a precipitate of Prussian blue, owing to reduction of the ferric salt (compare morphine).

A cold concentrated solution of sodium nitroprusside added to a solution of the hydrochloride precipitates reddish-coloured crystals. These are soluble in hot water, but again separate on cooling. The test is a good one to distinguish cocaine from morphine.

Urea and then strong H_2SO_4 added to the solid hydrochloride, and the whole strongly warmed, give a blue colour. Certain other organic nitrogen compounds, however, give a similar reaction.

Uranium nitrate solution containing a little potassium sulphocyanide (thiocyanate) gives an intense yellow precipitate in solutions containing 1 per cent. of the hydrochloride.

CONINE (Propyl-Piperidine), $C_5H_9(C_3H_7)NH$.

Conine is found in hemlock, and is one of the liquid alkaloids, of an oily nature, and having a powerful and disagreeable odour. It may be distilled, but undergoes some decomposition, in contact with air, but unchanged when distilled in an atmosphere of hydrogen. With steam or alcohol it may also be distilled. It is colourless when freshly distilled but darkens on keeping. It is optically active, being *dextro-rotatory*.

Conine is slightly soluble in water, readily soluble in alcohol, ether, and to some extent in chloroform. The salts are soluble in water and alcohol; hence when the salts (in solution) are decomposed by adding an alkali, the conine is set free, and, being even more insoluble in alkalies than water, oily drops of the alkaloid separate. On shaking with ether the alkaloid dissolves, and may be obtained by evaporation of the ether.

HCl gas (or vapour in a vessel rinsed out with strong HCl) gives a crystalline coating or deposit with conine.

HNO_3 (strong) gives only a faint red tint.

H_2SO_4 gives no colour immediately, but the mixture gradually becomes purple, and then green.

Br vapour also forms a mass of white crystals.

Cl water added to an aqueous solution of the alkaloid gives a white precipitate, soluble in HCl.

$AuCl_3$ (with solutions of the salts) gives a yellowish white precipitate, insoluble in HCl.

$PtCl_4$ gives no precipitate (distinction from nicotine).

$HgCl_2$ in solutions of the alkaloid—a white *amorphous* precipitate (compare nicotine).

Solution of sodium nitroprusside gives with dilute conine solutions, on standing or stirring, a red tint, which changes to yellow. The red tint disappears on warming, but appears again on cooling. (Distinction from nicotine.)

NICOTINE, $C_{10}H_{14}N_2$.

Nicotine is the alkaloid which occurs in tobacco, principally as the *malate*. It is a colourless liquid, but on exposure to air becomes brown. It has a disagreeable pungent odour. Distilled in air, some decomposition occurs, but it distils unchanged in hydrogen. It is also volatile with steam and alcohol. It is optically active (*lævo-rotatory*).

Nicotine is soluble in water, alcohol, ether, &c. The salts are readily soluble in water and alcohol. On adding an alkali to their solution the alkaloid separates, and may be obtained by dissolving out with ether.

SUMMARY OF ALKALI AND COLOUR REACTIONS OF NON-VOLATILE ALKALOIDS.

	KHO.	NaHCO₃ in Acid Solution.	Strong HNO₃.		Strong H₂SO₄.		H_2SO_4, then trace of HNO_3 (Erdmann).	Molybdic Acid (Frohde).	Fe_2Cl_6 and $K_3FeC_6N_6$.
			Cold.	On Heating.	Cold.	On Heating.			
Morphine .	Precipitate, soluble in excess.	Precipitate, insoluble in excess.	Yellowish red.	—	No colour.	Purple, then brown.	Violet to blood-red.	Violet, then green ; on stirring. deep blue.	Blue colour.
Narcotine .	Precipitate, insoluble in excess.	,,	Reddish yellow.	Yellow.	Greenish yellow.	Orange red, then violet.	Reddish violet or blood-red.	Green.	—
Quinine .	,,	,,	No colour.	? Yellow.	No colour.	Yellow, then brown.	No colour.	Pale green.	—
Cinchonine	,,	,,	,,	—	No colour.	Yellow, then black.	No colour.	No colour.	—
Strychnine	,,	No precipitate.	,,	—	No colour; on adding MnO₂, &c., blue, violet.	—	No colour.	No colour.	—
Brucine .	,,	,,	Blood-red (on adding SnCl₂, purple).	Yellow.	Pale rose.	—	Red colour.	Reddish.	—
Atropine .	,,	,,	No colour.	—	No colour.	—	No colour.	No colour.	—
Cocaine .	,,	,,	No colour.	—	No colour.	—	No colour.	No colour.	Blue colour.

APPENDIX IV.

TABLE SHOWING THE SOLUBILITY OF SALTS IN WATER AND ACIDS.

I. Names of Salts.	II. Soluble in Water.	III. Insoluble in Water, soluble in, or decomposed by, Acids.	IV. Insoluble in Water and Acids.
Carbonates	Alkali carbonates, and acid carbonates of Ba, Sr, Ca, Mg, Fe'', Mn, and Pb.	All other carbonates are decomposed by dilute acids, with evolution of CO_2. Spathose iron ore and dolomite are decomposed slowly.	None.
Sulphates	Most sulphates, with the exception of those mentioned in Columns III. and IV. (Ag_2SO_4 is difficultly soluble.)	A few basic sulphates, such as of Hg'', Hg'_2, $Fe'v$, Bi''', Sn''.	The sulphates of Ba, Pb, Sr, Ca, and the red chromic sulphate.
Sulphites.	Alkali sulphites, and the acid sulphites of the alkaline earthy metals.	All other sulphites are decomposed by acids (CO_2 and H_3BO_3 excepted), with evolution of SO_2.	None.
Hyposulphites.	Most hyposulphites are soluble in water (BaS_2O_3, $Ag_2S_2O_3$, and PbS_2O_3 are but little soluble).	All other hyposulphites are decomposed by acids, with evolution of SO_2 and separation of sulphur.	None.
Sulphides.	Alkali and alkaline earthy sulphides. (CaS and MgS are only sparingly soluble.)	All other sulphides are decomposed by HCl, with evolution of SH_2, or by HNO_3, or aqua regia, with separation of sulphur.	None.
Nitrates.	All nitrates, with the exception of a few basic nitrates (Bi, Hg).	A few basic nitrates, which are readily soluble in dilute HNO_3.	None.

TABLE SHOWING THE SOLUBILITY OF SALTS IN WATER AND ACIDS—*continued.*

I. Names of Salts.	II. Soluble in Water.	III. Insoluble in Water, soluble in, or decomposed by, Acids.	IV. Insoluble in Water and Acids.
Cyanates	The cyanates of the alkalies and alkaline earthy metals, also a few metallic cyanates, are soluble in water.	The few other cyanates known are decomposed by dilute HNO_3.	—
Sulphocyanates	The sulphocyanates of the alkali and alkaline earthy metals, also of Cu, Hg, Fe^{iv}, are soluble in water.	The few other characteristic sulphocyanates, *e.g.*, of 'Cu'$_2$, Ag, Hg$_2$, and Pb, are more or less readily decomposed by acids (HNO_3).	?
Formates	All formates are soluble in water, the Pb salt least so.	—	—
Acetates	All acetates are soluble in water. (Silver and mercurous acetates are difficultly soluble.) Also a few basic salts.	—	—
Benzoates	Benzoates of K, Na, Ba, Sr, Ca, Mg, and of Mn, Zn, Fe'', are soluble in water.	Ferric, cupric, silver, lead, mercurous and mercuric benzoates are soluble in acids.	—
Succinates	Most succinates are soluble in water.	Succinates of Fe^{iv}, Cu, Ag, Hg, and Pb dissolve readily in acids.	—
Oxalates	The alkali oxalates, as well as of Cr^{iv}; most others are insoluble or difficultly soluble in water.	All other common oxalates are soluble in acids. Calcium oxalate is insoluble in HCl.	—

Tartrates	The normal alkali tartrates are soluble in water, the acid less so than the normal salts.	The normal tartrates of the alkaline earths, earths and heavy metals are mostly difficultly soluble in water, but dissolve readily in mineral acids (HCl) and in tartaric acid.	
Citrates	The alkali citrates are soluble in water; most others are insoluble or difficultly soluble.	Citrates insoluble in water dissolve readily in acids.	?
Arsenates and Arsenites	The alkali arsenates and arsenites are soluble in water; most others are insoluble.	Arsenates and arsenites insoluble in water dissolve in acids, and frequently also in ammonium salts.	None.
Chromates	The chromates of the alkalies, as well as of Sr, Ca, Mg, Zn, Mn, Fe^{v}, Cu, are soluble in water.	All chromates insoluble in water dissolve in acids (in concentrated HCl) with evolution of chlorine, and in concentrated H_2SO_4 with liberation of oxygen.	Ignited lead chromate. Native chrome iron.

The physical state of a substance has a great influence on its solubility in different solvents, more especially on the rate of solution. A substance that has been ignited is generally less easily dissolved than before ignition, probably because in many cases ignition makes a substance denser. This applies to many oxides, oxy salts, and salts which fuse without decomposition. Al_2O_3 and SnO_2, for instance, as emery or ruby, or tinstone, are absolutely insoluble in acids.

APPENDIX V.

UNFORTUNATELY from time to time several methods of writing the formulæ of chemical substances have been proposed and partly adopted; consequently there are several modes in use, empirical, structural or constitutional, and graphic. All these are useful under certain circumstances. Structural formulæ are almost a necessity when dealing with so-called organic compounds. And, further, it is quite correct to use them always with organic compounds, as in most cases they represent at least one way in which the organic compound can be built up or synthetised. With minerals this is seldom the case; we know little of the "structure" of minerals excepting by analogy. It is, however, desirable that we should, wherever possible, express in a formula the constitution of the compound, for that will, or should, exhibit how and in what manner it will react with another substance.

The formulæ used in this book are, as far as minerals are concerned, empirical, showing only the number of atoms of any particular element united together, and generally the *least possible* number.

By the adoption of a somewhat arbitrary arrangement most of these empirical formulæ may be converted into a "structural" one, in which one idea, at any rate, of the constitution of the substance may be exhibited, and the same number of atoms indicated as taking a part by the purely empirical formulæ still retained. Again, from these "structural" formulæ graphic may be formed, by arranging the atoms in space with regard to each other, so that, as far as we at present know, the element in a compound with the greatest "fixing" or combining power for other elements, taking its power in this respect for hydrogen as unity, is considered as the dominating element; and its affinities must be first satisfied before those of other elements come into play.

This may be a correct assumption or only partially so.

The ordinary formula for sulphuric acid is H_2SO_4. It is alone used in this book for simplicity. The action of peroxide of hydrogen on SO_2 shows that it may be considered as $SO_2(OH)_2$. When SO_3 comes in contact with water, H_2O, a direct union, as far as we can see, takes place, and hence the constitution would be H_2OSO_3,

presence of water, on sulphuric acid is to expel two hydrogen atoms, which might point to its being H_2SO_4. The action of SO_2 on PbO_2 or MnO_3 results in the formation of $PbSO_4$, or $MnSO_3$, a similar case to the first example. The action, again, of dry H_2SO_4 on NaCl, whereby $NaHSO_4$ and HCl are formed, points to the constitution $H.SO_3.OH$. The electrolytic decomposition *may* point to H_2SO_4, but the action is probably very complex.

Several compounds of oxides of sulphur with chlorine, with oxides of nitrogen, or even with HCl, are known, and their method of formation points to the existence of the group HO in the acids of sulphur, and also in most, if not, all, other so-called oxy acids or negative hydrates like nitric or phosphoric acid. The action of PCl_5 and $POCl_3$ on some of these acids, as H_2SO_4, also, by analogy with the actions of these reagents on alcoholic and similar compounds, points to the existence of HO in combination.

The compounds PCl_3, PCl_5, and $POCl_3$ act on water thus:

$$PCl_3 + H_2O = POCl + 2HCl; \quad PCl_5 + H_2O = POCl_3 + 2HCl, \&c.$$

On alcohol, C_2H_5OH, thus:

$$PCl_5 + C_2H_5OH = POCl_3 + HCl + C_2H_5Cl.$$

Also on acetic acid:

$$CH_3COOH + PCl_5 = POCl_3 + HCl + CH_3COCl.$$
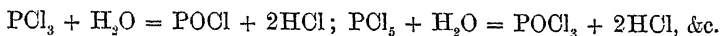
Also $POCl_3$ on sulphuric acid:

$$2SO_2{OH \atop OH} + POCl_3 = 2SO_2{Cl \atop OH} + HCl + HPO_3.$$
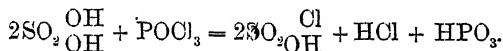
It will be seen from this that great difficulties exist in ascertaining the real structure of mineral compounds as yet; but it does no harm whatever to form a mental picture of the possible structure of these substances, keeping as close to experimental facts as possible.

The following table is therefore arranged so that from the probable constitution of the acid that of the salt may be expressed.

The metallic bases are distinguished as monad, dyad, triad, tetrad, pentad, and hexad, the acid representing the monad combination being in the first column.

Other metals are represented by M'', M''', M^{iv}, M^v, M^{vi}. In addition to the normal salts, various other constitutional formulæ of mixed and basic compounds are given. The basicity of the acid is placed in brackets after its empirical formula.

Acid.	Structural Formula.	Dyad Salts.	Triad Salts.	Tetrad Salts.	Pentad Salts.	Hexad Salts.
			Nitric Acid.			
HNO_3 (1)	NO_2HO	$\begin{Bmatrix} NO_2\ M''O_2 \\ NO_2 \\ or \\ N_2O_4M''O_2 \end{Bmatrix}$	$\left.\begin{array}{l} NO_2 \\ NO_2 \\ NO_2 \end{array}\right\} M'''O_3$ or $N_3O_6M\ O_3$	$(NO_2)_4M^{iv}O_4$	$(NO_2)_5M^vO_5$	$(NO_2)_6M^{vi}O_6$

Ferric nitrate (pseudo-triad), $Fe_2N_6O_{18} = (NO_2)_6Fe_2O_6$. Mercurous nitrate, $Hg_2N_2O_6 = (NO_2)_2\cdot Hg_2O_2$.

Nitrous Acid.

Normal nitrites are written as nitrates, but the group (NO) is substituted for (NO_2).

			Carbonic Acid.			
H_2CO_3 (2)	$CO(HO)_2$	$COM''O_2$	$(CO)_3(M'''O_3)_2$	$(CO)_2M^{iv}O_4$	$(CO)_5(M^vO_5)_2$	$(CO)_6M^{vi}O_6$
			Sulphuric Acid.			
H_2SO_4 (2)	$SO_2(HO)_2$	$SO_2M''O_2$	$(SO_2)_3(M'''O_3)_2$	$(SO_2)_2M^{iv}O_4$	$(SO_2)_5(M^vO_5)_2$	$(SO_2)_6M^{vi}O_6$

Sulphurous Acid, $SO(HO)_2$.

Normal sulphites are written as sulphates, but the group (SO) is substituted for (SO_2).

			Phosphoric Acid.			
H_3PO_4 (3)	$PO(HO)_3$	$(PO)_2(M''O_2)_3$	$(PO)_3M'''O_3$	$(PO)_4(M^{iv}O_4)_3$	$(PO)_5(M^vO_5)_2$	$(PO)_2M^{vi}O_6$
			Silicic Acid (Ortho).			
H_4SiO_4 (4)	$Si(HO)_4$	$Si(M''O_2)_2$	$Si_3(M'''O_3)_4$	$Si(M^{iv}O_4)$	$Si_5(M^vO_5)_4$	$Si_3(M^{vi}O_6)_2$

From the above examples, in which the structural formulæ of mono-, di-, tri- and tetra-basic acids are given, it will be found easy to deduce general rules for making structural formulæ for all salts, especially if the relative proportion of the metal to the negative element is carefully noticed.

The examples are given only in the case of normal salts; but it will be found simple, if they are well remembered, to construct constitutional formulæ for any acid or basic salt, and from these graphic formulæ.

Examples of Graphic Formulæ.

Ferric sulphate.

$$HS_2O_4 = H-O-S-OH$$

$H_4SiO_4.$

Felspar.

$$Si_6O_{16}K_2Al_2 =$$

See also in the text the nucleus group formulæ proposed for some double salts, as the chloroplatinates and others.

Many points in this connection are waiting for further investigation.

Acid.	Structural Formula.	Dyad Salts.	Triad Salts.	Tetrad Salts.	Pentad Salts.	Hexad Salts.
			Nitric Acid.			
HNO_3 (1)	NO_2HO	$\left\{\begin{array}{l} NO_2\,M''O_2 \\ NO_2 \\ \text{or} \\ N_2O_4M''O_3 \end{array}\right.$	$\left\{\begin{array}{l} NO_2 \\ NO_2M'''O_3 \\ NO_2 \\ \text{or} \\ N_3O_6M\ O_3 \end{array}\right.$	$(NO_2)_4M^{iv}O_4$	$(NO_2)_5M^vO_5$	$(NO_2)_6M^{vi}O_6.$

Ferric nitrate (pseudo-triad), $Fe_2N_6O_{18} = (NO_2)_6Fe_2O_6.$ Mercurous nitrate, $Hg_2N_2O_6 = (NO_2)_2Hg_2O_2.$

Nitrous Acid.

Normal nitrites are written as nitrates, but the group (NO) is substituted for (NO_2).

			Carbonic Acid.			
H_2CO_3 (2)	$CO(HO)_2$	$COM''O_2$	$(CO)_3(M'''O_3)_2$	$(CO)_2M^{iv}O_4$	$(CO)_5(M^vO_5)_2$	$(CO)_6M^{vi}O_6.$
			Sulphuric Acid.			
H_2SO_4 (2)	$SO_2(HO)_2$	$SO_2M''O_2$	$(SO_2)_3(M'''O_3)_2$	$(SO_2)_2M^{iv}O_4$	$(SO_2)_5(M^vO_5)_2$	$(SO_2)_6M^{vi}O_6.$

Sulphurous Acid, $SO(HO)_2$.

Normal sulphites are written as sulphates, but the group (SO) is substituted for (SO_2).

			Phosphoric Acid.			
H_3PO_4 (3)	$PO(HO)_3$	$(PO_2)_2(M''O_2)_3$	$(PO)_2M'''O_3$	$(PO)_4(M^{iv}O_4)_3$	$(PO)_5(M^vO_5)_2$	$(PO)_2M^{vi}O_6.$
			Silicic Acid (Ortho).			
H_4SiO_4 (4)	$Si(HO)_4$	$Si(M''O_2)_2$	$Si_3(M'''O_3)_4$	$Si(M^{iv}O_4)$	$Si_5(M^vO_5)_4$	$Si_3(M^{vi}O_6)_2.$

From the above examples, in which the structural formulæ of mono-, di-, tri- and tetra-basic acids are given, it will be found easy to deduce general rules for making structural formulæ for all salts, especially if the relative proportion of the metal to the negative element is carefully noticed.

The examples are given only in the case of normal salts; but it will be found simple, if they are well remembered, to construct constitutional formulæ for any acid or basic salt, and from these graphic formulæ.

Examples of Graphic Formulæ.

Ferric sulphate.

$$HS_2O_4 = H-O-S-OH$$

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$$Si_6O_{16}K_2Al_2 =$$

See also in the text the nucleus group formulæ proposed for some double salts, as the chloroplatinates and others.

Many points in this connection are waiting for further investigation.

APPENDIX VI.

It is most particularly recommended that all reagents be made up for the use of students as equivalent solutions. There is no difficulty whatever in carrying this out, and the advantage in practical teaching is very great. Approximately equal volumes of reagent solutions will then react completely, or neutralise each other.

The tendency is generally to take too much for an analysis, and be in consequence working with very concentrated solutions and precipitates it is difficult to wash properly. An equivalent reagent solution will be found to help most speedily in correcting this.

These remarks appeared in a previous edition. Extended trial has further proved their advantages over the ordinary uncertain, indeed unknown, solutions. An additional table is given after this one, slightly modified from Mr. Reddrop's paper in the *Chemical News* (No. 1591).

REAGENTS.

SOLVENTS.

Distilled Water.*— Obtained by condensing steam by means of a tin worm. The first portions of the condensed water usually contain carbon di-oxide and ammonium carbonate, and should be rejected.

Impurities.—When evaporated in a platinum vessel, distilled water should not leave a solid residue, either organic or mineral. Ammonium sulphide ought not to give a precipitate (Cu, Pb, Fe), neither ought basic lead acetate to cause a turbidity (CO_2, $(NH_4)_2CO_3$). No turbidity or precipitate should be produced on the addition of ammonium oxalate (lime), barium chloride (sulphates), or silver nitrate (chlorides). Pure distilled water is colourless, inodorous, and tasteless.

Water used for Nessler's test should be specially distilled in a glass retort with a few pieces of KHO and a little potassium permanganate, and the distillate rejected as long as the Nessler solution indicates any traces of ammonia.

* The asterisk marks the more important reagents.

ALCOHOL (METHYLATED SPIRIT), C_2H_5HO or $EtHO$.—Ordinary methylated spirit (*i.e.*, ethylic alcohol, 90 per cent.), may be employed for most purposes. It can be rendered practically absolute by shaking with well-dried potassium carbonate, and distilling the clear spirit in a flask or retort from a water-bath.

Impurities.—Commercial methylated spirit frequently leaves a residue on evaporation; if so, it should be rectified by distillation. It should be without action on litmus papers.

ETHER.—Ordinary ether (methylated, *i.e.*, prepared from methylated alcohol) of commerce is pure enough. It should be kept over dried K_2CO_3 in a bottle.

ACIDS.

SULPHURIC ACID,* H_2SO_4.—Common oil of vitriol may be used in all operations with which its usual impurities (lead, arsenic, iron, lime, nitric acid) do not interfere. Sulphuric acid, free from arsenic, should be employed for generating arsenious or antimonious hydride, and an acid free from lead, whenever this metal has to be precipitated as sulphate. Sulphuric acid, free from nitric acid and nitric peroxide, must be employed in testing for nitric acid by means of ferrous sulphate.

Impurities.—Pure sulphuric acid is colourless, and leaves no residue on evaporation in a porcelain dish. When a solution of ferrous sulphate is poured upon it in a narrow test-tube it should not form a brown ring where the two liquids come in contact (nitric acid and nitric peroxide), nor strike a blue colour when a highly diluted solution of the acid is added to a solution of pure potassium iodide and starch paste (nitrous acid). The presence of arsenic is best ascertained by passing a current of sulphuretted hydrogen through the dilute acid, or by generating hydrogen from zinc free from arsenic, and passing the gas through an ignited combustion tube (*see* Marsh's test). Lead sulphate is frequently found in sulphuric acid, and is precipitated on diluting with water, as it is less soluble in dilute than in concentrated acid. Hydrochloric acid should cause no turbidity (lead) where the two liquids meet.

The pure acid can readily be bought, and the student need not attempt to purify the crude acid.

DILUTE SULPHURIC ACID.*—Prepare by pouring slowly one part by measure of the concentrated acid (sp. gr. 1·8) into five parts by measure of distilled water, with continuous stirring. Thin glass vessels (beakers), or a porcelain dish, should be employed, as much heat is evolved. Allow the lead sulphate to subside, and decant or syphon off the clear liquid.

NITRIC ACID (AQUA FORTIS), HNO_3.—Should be colourless, and leave no residue on evaporation in a glass dish.

Impurities.—Sulphuric and hydrochloric acid. Dilute considerably, and test portions with barium nitrate and silver nitrate.

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DILUTE NITRIC ACID.*—Prepared by diluting one part of pure commercial acid (sp. gr. 1·38 to 1·45) with three parts of distilled water.

CRUDE NITRIC ACID.*—May be employed for all experiments in which the above impurities do not interfere, *e.g.*, in the preparation of N_2O_2 or N_2O_3 by the action of nitric acid upon copper or arsenious anhydride.

CONCENTRATED HYDROCHLORIC ACID,* MURIATIC ACID, HCl.—Should be colourless, and leave no residue on evaporation.

Impurities.—Ferric chloride, sulphurous and sulphuric acids, arsenic. The dilute acid should not impart a blue colour to a solution of KI and starch paste (Cl or Fe_2Cl_6).—On adding a few drops of a solution containing iodide of starch, the blue colour should not be destroyed (SO_2). The dilute acid should remain clear on the addition of a solution of barium chloride (H_2SO_4). Sulphuretted hydrogen, when passed through the dilute acid should not produce a precipitate (arsenic), nor should ammonium sulphocyanate redden the diluted acid (iron).

CRUDE HYDROCHLORIC ACID.*—Should be employed whenever the impurities which it contains do not interfere with the object in view—as, for instance, in the preparation of chlorine from manganic dioxide.

AQUA REGIA OR NITROHYDROCHLORIC ACID.—Prepared, when required only, by mixing one part of concentrated nitric acid with three to four parts of hydrochloric acid.

SULPHUROUS ACID, H_2SO_3.—Prepared by acting with concentrated sulphuric acid upon copper, and passing the gas into water. The solution should be kept in a well-stoppered bottle.

CARBONIC ACID WATER.—A solution is prepared by acting with hydrochloric acid upon marble, and passing the evolved carbon dioxide into water.

CHLORINE WATER.—A solution of chlorine in water is readily prepared. It should be kept in a well-stoppered bottle, and in a dark place, since on exposure to light it is speedily converted into HCl, with evolution of oxygen.

ACETIC ACID,* $\begin{cases} CH_3 \\ COOH \end{cases}$—It should leave no residue on evaporation.

Impurities.—Sulphuric and hydrochloric acids, lead, copper, iron, lime.

TARTARIC ACID, $C_4H_6O_6 = T(\overset{\frown}{HO})_2$.—A solution is prepared when required only, as the acid undergoes decomposition in an aqueous solution.

Impurities.—Tartaric acid contains sometimes gypsum and

calcium tartrate, which are best tested for by igniting a few crystals on platinum, extracting the residue, if any, with a few drops of dilute HCl, and adding to one portion $BaCl_2$, to another ammonia and ammonium oxalate.

OXALIC ACID, $H_2C_2O_4$.—The commercial acid is sufficiently pure. It should not leave more than a trace of a residue on ignition.

Impurities.—Iron, potassium and sodium oxalates, lime.

HYDROFLUORIC ACID, HF.—A solution stored up in a gutta-percha bottle is best bought, as its preparation involves expensive apparatus. It should leave no fixed residue on evaporation to dryness.

HYDROFLUOSILICIC ACID, $2HF,SiF_4$.—A solution of this acid in water is prepared as described under silicates, &c. It should be made sufficiently strong readily to precipitate a soluble barium salt.

Impurities.—Owing to the mode of preparation the acid is often contaminated with sulphuric acid. It should not produce a precipitate in a solution of a strontium salt.

HYDROSULPHURIC ACID, SH_2.—Prepared when required. In well-appointed laboratories sulphuretted hydrogen is now usually stored in a gasholder over oil, and supplied like coal gas from small taps, in closets, connected with the chimney. The gas, whether obtained from a constant generating apparatus or from a gasholder, should invariably be passed through a wash-bottle containing water. A saturated solution of sulphuretted hydrogen in water answers most purposes of the analyst. It should be kept in a well-stoppered bottle, since sulphuretted hydrogen decomposes rapidly when in contact with air, with formation of sulphur acids and precipitation of white sulphur.

If the gas be required entirely free from AsH_3, it should be generated by acting with pure HCl (concentrated) upon native *grey antimony*, Sb_2S_3.

BASES AND METALS.

POTASSIUM HYDROXIDE,* KHO, or SODIUM HYDROXIDE, NaHO.—Usually obtained in commerce in the form of sticks or lumps.

Impurities.—Silica, alumina, phosphoric, sulphuric, and hydrochloric acids (sulphates and chlorides, often in not inconsiderable quantities), and carbonic acid. On dissolving in water, and allowing the suspended matter to subside, the clear solution may be syphoned off.

Pure sodium hydroxide is indispensable for the separation of alumina from the oxides of iron and chromium.

AMMONIUM HYDROXIDE,* NH_4OH.—The *liquor ammonii caustici* of commerce has a sp. gr. ·88.

Impurities.—A solution of ammonia should be colourless; on neutralising with pure HCl it should remain inodorous. When evaporated in a glass or platinum dish it should not leave any residue. Ammonia frequently contains traces of sulphuric and hydrochloric acids, and sometimes not inconsiderable quantities of ammonium carbonate, when it will produce a white precipitate on the addition of lime-water, and sometimes other bases.

BARIUM HYDROXIDE,* $Ba(HO_2)$.

Impurities.—The solution commonly called baryta-water should, on precipitating with pure H_2SO_4, give a filtrate which leaves no fixed residue on evaporating to dryness in a platinum vessel.

CALCIUM HYDROXIDE,* $Ca(HO)_2$.—Freshly slaked lime in powder is used in qualitative analysis, as well as a solution of lime, so-called lime-water. This is prepared by dissolving in cold distilled water some freshly slaked lime, allowing to subside in a stoppered bottle, and syphoning off the clear liquid into another bottle.

AMMONIUM SULPHIDE,* $(NH_4)_2S$.—Prepared by saturating three parts of ammonium hydroxide with sulphuretted hydrogen gas, whereby $SHNH_4$ is formed. On diluting this solution of hydrogen ammonium sulphide with two parts of ammonium hydroxide, a sulphide is obtained which contains a little free ammonia. The concentrated solution may be diluted with ten times its bulk of water. It should be kept in well-stoppered bottles. Calcium or magnesium salts should not be precipitated; nor should the solution leave a residue on evaporation and ignition. The oxygen of the air decomposes it gradually into NH_3, OH_2, and yellow ammonium sulphide $= (NH_4)_2S_n$.

YELLOW AMMONIUM SULPHIDE.—Used for the solution and conversion of SnS into SnS_2. It may be prepared by digesting the neutral $(NH_4)_2S$ with flowers of sulphur, and filtering the liquid.

SODIUM SULPHIDE, SNa_2.—Prepared by saturating one portion of a solution of sodium hydroxide with sulphuretted hydrogen, and adding it to the second portion. A little ferrous sulphide, which is generally precipitated, is filtered off. The solution must be kept in a well-stoppered bottle.

SODA-LIME AND CHARCOAL.—This is a most useful reagent for ammonia, mercury, arsenic, cadmium, in the dry way. Mix two parts CaO with one part NaHO and one of charcoal, moisten with water and mix thoroughly into a paste; place in a covered clay crucible, and dry thoroughly in an oven; pound up, and keep closely

SALTS.

HYDROGEN DISODIUM PHOSPHATE,* $HNa_2PO_4 + 12Aq.$—Recrystallise the commercial salt.

Impurities.—Sulphate and chloride. Ammonium hydroxide should not cause any turbidity on warming (alkaline earthy phosphates).

SODIUM ACETATE, $\left\{ \begin{array}{l} CH_3 \\ CONa \end{array} \right. + 6Aq.$ The commercial salt generally contains sodium sulphate. If a pure salt cannot be procured, sodium acetate may be prepared by neutralising pure sodium carbonate with pure acetic acid.

SODIUM HYPOCHLORITE, $ClNaO.$—Prepared by shaking up one part of bleaching powder with ten parts of water, and adding a saturated solution of commercial sodic carbonate as long as a precipitate is produced. Allow to subside, and syphon off.

AMMONIUM OXALATE.*—Purify the commercial salt by recrystallisation.

Impurities.—The salt should leave no fixed residue on ignition. Sulphuretted hydrogen or ammonium sulphide ought not to produce a turbidity or a precipitate.

AMMONIUM CARBONATE.*

Impurities.—Iron, lead, sulphuric and hydrochloric acids. The salt should volatilise completely, and give no precipitate with barium chloride or silver nitrate (after acidulating with hydrochloric or nitric acid respectively), also no precipitate with sulphuretted hydrogen or ammonium sulphide.

HYDROGEN AMMONIUM CARBONATE, $NH_4HCO_3.$—Obtained in colourless rhombic prisms, on passing carbonic anhydride to supersaturation into a concentrated solution of ammonia. The salt is employed for the separation of As_2S_3 from Sb_2S_3 and SnS_2. A saturated solution is prepared when required.

AMMONIUM CHLORIDE.*—The commercial salt (sal ammoniac) usually contains iron. Purify by adding to the solution a little ammonium hydroxide. Allow the ferric hydroxide to subside, and neutralise the alkaline filtrate exactly with pure HCl. The salt should leave no fixed residue on ignition.

AMMONIUM MOLYBDATE.—This salt may be purchased. It is dissolved in strong ammonium hydroxide and allowed to stand for some time. A slight yellow precipitate, containing ferric hydroxide, usually subsides. The clear fluid is poured into concentrated nitric acid as long as the molybdic acid which at first precipitates is entirely redissolved. The nitric acid solution should remain colourless on

boiling. A yellow precipitate indicates contamination with phosphoric acid, and the reagent should not be used till it remains clear on digestion.

AMMONIUM SULPHATE.—Recrystallise the commercial salt from an ammoniacal solution in order to separate iron. Keep a saturated solution for use.

AMMONIUM NITRATE, NH_4NO_3.—The commercial salt is recrystallised and dissolved, when required, to a saturated solution. It should leave no residue when ignited on platinum.

BARIUM CHLORIDE,* $BaCl_2 + 2Aq$.—The commercial salt is rarely pure enough, and not infrequently contains lead. It should not give a precipitate with sulphuretted hydrogen or ammonium sulphide, nor should a residue be left after precipitating the whole of the barium by pure sulphuric acid and evaporating the filtrate in a platinum dish. Purify, if necessary, by passing a current of sulphuretted hydrogen, filtering, and recrystallising.

BARIUM NITRATE, $Ba(NO_3)_2$.—Should not be precipitated by silver nitrate, as it is sometimes employed, instead of barium chloride, in order to avoid introducing any chlorine into a solution. Pure barium acetate answers the same purpose. For other impurities, test as for barium chloride.

BARIUM CARBONATE, $BaCO_3$.—Prepared by precipitation of pure barium chloride with ammonium carbonate and hydroxide. Wash well till free from NH_4Cl, stir up the precipitated barium carbonate with water to a thick, creamy consistency, and keep it for use in a stoppered bottle. Shake up before using this reagent.

CALCIUM CHLORIDE,* $CaCl_2 + 6Aq$.—The solution should be neutral to test-papers, and should not be precipitated by ammonium sulphide (iron).

CALCIUM SULPHATE, $CaSO_4$.—A saturated solution is prepared by repeatedly shaking up gypsum with water, allowing to subside, and syphoning off the clear liquid.

MAGNESIUM SULPHATE.—The commercial salt ($MgSO_4OH_2 + 6Aq$.). Recrystallise.

FERROUS SULPHATE.—The commercial salt, $FeSO_4 + 7OH_2$, is pure enough.

FERRIC CHLORIDE,* Fe_2Cl_6.—Prepared by dissolving freshly precipitated and well washed $Fe_2(HO)_6$ in pure HCl, keeping the ferric hydroxide in excess.

SILVER NITRATE,* $AgNO_3$.—Prepared either from silver (pure)

acid, and precipitation as AgCl. Filter off the copper salt, and wash thoroughly with hot water; transfer to a porcelain dish, and introduce clean strips of zinc. Collect the finely divided silver on a filter, wash thoroughly with hot water acidulated with a little sulphuric acid, and dissolve in dilute nitric acid. Evaporate the solution to dryness, and fuse the residue gently.

NESSLER'S SOLUTION.—Dissolve 3·5 grms. of KI in 10 c.c. of water; next dissolve 1·6 grm. of $HgCl_2$ in 30 c.c. of water; add the mercury solution gradually and with continuous agitation to the solution of potassium iodide, until the precipitate ceases to be redissolved; then add 60 c.c. of potassium hydroxide and filter. Keep in a small bottle, out of contact with ammonia fumes.

This reagent is of great value for the detection of mere traces of ammonia.

CUPRIC SULPHATE.—The commercial salt ($CuSO_4 + 5Aq.$) is purified by repeated crystallisation.
Impurities.—Iron, zinc.

CUPROUS CHLORIDE, Cu'_2Cl_2.—Obtained by digesting $CuCl_2$ with metallic copper and HCl.

STANNOUS CHLORIDE, $SnCl_2$.—Prepared by boiling pure granulated tin in concentrated HCl, with the aid of a piece of platinum foil. Keep the filtered solution over granulated tin in a small stoppered bottle. It is best made as wanted in a test-tube.

AURIC CHLORIDE, $AuCl_3$.—Prepared by dissolving pure gold in aqua regia, evaporating to dryness on a water-bath and dissolving in water.

PLATINIC CHLORIDE, $PtCl_4$.—Dissolve some platinum scraps in aqua regia. Precipitate with NH_4Cl. Collect precipitate on a Swedish filter-paper; wash with strong alcohol; dry and ignite in a porcelain crucible, gently at first, and lastly to intense redness. Redissolve the spongy platinum in aqua regia. Evaporate repeatedly to dryness on a water-bath, with addition of HCl. Pure platinic chloride should dissolve completely in pure alcohol.

Zinc, free from arsenic, granulated, and in the form of strips or sticks.

Iron (steel), Copper, Tin, Lead, Platinum (used in the form of wire, bars, sheets, turnings), and Mercury can be obtained of sufficient purity for the purposes of qualitative analysis.

METALLIC LEAD FREE FROM SILVER.—Prepared by precipitation of lead acetate by metallic zinc, washing with hot water, then alcohol, and melting in a dry crucible.

PLUMBIC DIOXIDE, PbO_2.—Readily prepared by digesting red lead in boiling dilute nitric acid. The brown powder is well washed by decantation, and lastly on the filter.

MANGANIC DIOXIDE, MnO_2.—Use the powdered commercial black oxide.

HYDROGEN PEROXIDE, O_2H_2, or $(HO)_2$.—A solution may be prepared by passing a current of carbon dioxide through water in which barium peroxide is suspended. The precipitated barium carbonate is filtered off. The commercial article usually contains a little free mineral acid, such as HCl or H_2SO_4, added in order to prevent its spontaneous decomposition. Hydrofluosilicic acid is also sometimes met with, used probably (in excess) to remove any soluble barium salt.

Reagents used for Fusions and for Blowpipe Reactions.

SODIUM CARBONATE,* Na_2CO_3.—Should be free from sulphate and chloride.

FUSION MIXTURE,* OR WHITE FLUX.—Consisting of dry Na_2CO_3 and K_2CO_3, mixed in the proportion of their combining weights, *i.e.*, $106 + 138$, or in the proportion of 10 to 13.

Pure carbonates free from silica, chlorides, and sulphates, should be procured, as their purification cannot be effected without using silver and platinum vessels.

Black Flux.—Prepared by igniting crystals of Rochelle salt (potassio-sodium tartrate) in a platinum or iron crucible. The residue consists of carbon and alkali carbonates.

MICROCOSMIC SALT,* $NH_4NaPO_4 + 8Aq$.—The salt should be dried, and used in the form of a powder. On being heated in a loop of platinum wire it is converted into $NaPO_3$.

POTASSIUM CYANIDE,* KCy.—Exceedingly useful for reducing metallic oxides and sulphides, either in the crucible or on charcoal. For blowpipe reactions a mixture of equal parts of KCy and Na_2CO_3 (or fusion mixture) is preferable, because it sinks readily into the charcoal, and yields metallic globules of great purity. For the separation of Ni and Co the salt is dissolved, when required, in twenty parts of cold water, as its aqueous solution is rapidly decomposed.

POTASSIUM NITRATE,* KNO_3.—Used as an oxidising agent. The commercial salt should be purified by dissolving the crystals in hot water to a saturated solution, and allowing to cool in a porcelain dish with continuous stirring. The nitrate falls out first as a fine white powder, "meal nitre," and the impurities—*e.g.*, phosphate, sulphate, or chloride—are left in the mother-liquor.

POTASSIUM CHLORATE,* $\begin{cases} OCl \\ OKO \end{cases}$.—This salt can readily be obtained pure—*i.e.*, free from chloride. Either by itself or in conjunction with hydrochloric acid, it serves as a powerful oxidising agent.

BORAX,* $B_4O_5(NaO)_2$ or $Na_2B_4O_7 + 10Aq$.—The crystals should be gently heated in a platinum crucible till the water of crystallisation has been driven off, and the mass kept powdered and ready for use in blowpipe reactions.

HYDROGEN POTASSIUM SULPHATE, $KHSO_4$.—Prepared by heating in a platinum dish 87 parts of normal potassium sulphate with ·49 parts of pure sulphuric acid, till the clear mass fuses steadily. Pour out on a porcelain slab, and keep the lumps in a bottle.

COBALTOUS NITRATE, $Co(NO_3)_2$.—Used in solution only. Should be free from other metals. It is best to dissolve the nitrate in hot water, saturate with ammonia, and either expose to air or add a few drops of H_2O_2. After it has formed a brown solution, filter, and neutralise with nitric acid.

Vegetable Colouring-Matters—Test-Papers.

Litmus Solution.—Digest the small pieces of commercial litmus with pure water until a strong purple-blue solution is formed, and filter. It should be diluted so that one drop of reagent—diluted HCl—added to a litre will turn it red, and a similar quantity of NH_4OH turn it blue. Litmus paper is made by immersing filter paper in above solutions, and drying out of contact with acid or ammonia fumes.

Turmeric Paper.—Prepared by digesting at a gentle heat one part of turmeric root with six parts of alcohol. Filter and soak strips of porous paper with the yellow extract. The dried papers should exhibit a fine yellow tint. Like litmus papers, they serve for the detection of free alkalies. All test-papers should be kept in well-stoppered bottles or wooden boxes.

Indigo Solution.—Prepared by gradually stirring four to six parts of fuming sulphuric acid into one part of finely divided indigo, and allowing the mixture to stand for forty-eight hours before pouring into it twenty parts of water. Filter, and keep for use in a dark place. The solution of indigo is used for detecting nitric acid, chloric acid, and free chlorine, owing to the formation of products of oxidation of a yellow colour.

A considerable number of organic substances have been proposed as colour reagents in the same sense as litmus—that is, for distinguishing the point where acidity ends or where alkalinity begins.

Some of these are mentioned in the Appendix on Volumetric Analysis.

Name of Reagent.	Symbol.	Molecular weight.	Equivalent weight.	Equivalent System. Grms. per litre.	Strength.
Sulphuric Acid	H_2SO_4	98	49	—	36N
,,	,,	,,	,,	—	5N
,,	,,	,,	,,	49	N
Nitric Acid	HNO_3	63	63	—	24N
,,	,,	,,	,,	—	16N
,,	,,	,,	,,	—	5N
,,	,,	,,	,,	63	N
Hydrochloric Acid	HCl	36·5	36·5	—	10N
,,	,,	,,	,,	—	5N
,,	,,	,,	,,	36.5	N
Sulphurous Acid	H_2SO_3	82	41	—	4N
Carbonic Acid	H_2CO_3	62	31	—	$\dfrac{N}{10}$
Acetic Acid	$HC_2H_3O_2$	60	60	—	17N
,,	,,	,,	,,	—	5N
,,	,,	,,	,,	60	N
Tartaric Acid	$H_2C_4H_4O_6$	150	75	—	5N
,,	,,	,,	,,	75	N
Citric Acid	$H_3C_6H_5O_7$	192	64	—	5N
,,	,,	,,	,,	64	N
Oxalic Acid	$H_2C_2O_4$	90	45	—	$\dfrac{3N}{2}$
Hydrofluoric Acid	HF	20	20	—	12N ?
Hydrofluosilicic Acid	H_2SiF_6	144	72	—	N
,,	,,	,,	,,	—	
Hydrogen Sulphide	H_2S	34	17	—	$\dfrac{N}{4}$
Chlorine Water	Cl_2	71	35·5	—	$\dfrac{N}{5}$
Bromine	Br_2	160	80	—	37N
Bromine Water	,,	,,	,,	—	$\dfrac{N}{2}$
Hydrogen Peroxide	H_2O_2	34	17	—	4N
				—	2N
Potassium Hydroxide	KHO	56	56	—	5N
				56	N
Sodium Hydroxide	$NaHO$	40	40	—	5N
				40	N
Ammonium Hydroxide	NH_4OH	35	35	—	20N
,,	,,	,,	,,	—	5N
,,	,,	,,	,,	35	N
Barium Oxide	BaO	153	76·5	—	$\dfrac{N}{3}$
Calcium Oxide	CaO	56	28	—	$\dfrac{N}{20}$
Ammonium Sulphide	$(NH_4)_2S$	68	34	—	5N

Symbol of Substance taken.	Method of Preparing Reagent.
—	Sulphuric acid, sp. gr. 1·8427 at 15·5° C.
—	Sulphuric acid diluted to sp. gr. 1·1527 at 15·5°.
—	200 cc. of 5 N sulphuric acid diluted to 1 litre.
—	Nitric acid sp. gr. 1·50.
—	Nitric acid sp. gr. 1·4268 at 15·5° C.
—	Nitric acid diluted to sp. gr. 1·1656 at 15·5° C.
—	280 c.c. of 5 N nitric acid diluted to 1 litre.
—	Hydrochloric acid sp. gr. 1·1611 at 15·5° C.
—	Hydrochloric acid diluted to sp. gr. 1·0843 at 15·5° C.
—	200 c.c. of 5 N hydrochloric acid diluted to 1 litre.
—	Water at 15·5° C. saturated with sulphur dioxide (sp. gr. 1·052).
—	Water at 15·5° C. saturated with carbon dioxide.
—	Acetic acid solid at 10° C.
—	294 c.c. of 17 N acetic acid diluted to 1 litre.
—	200 c.c. of 5 N acetic acid diluted to 1 litre.
$H_2C_4H_4O_6$	375 grms. dissolved and diluted to 1 litre.
	75 ,, ,, ,,
$H_3C_6H_5O_7,Aq$	350 ,, ,, ,,
,,	70 ,, ,, ,,
$H_2C_2O_4,2Aq$	94·5 ,, ,, ,,
—	Hydrofluoric acid, sp. gr. 1·15 ?
—	Water at 15·5° C. saturated with hydrogen sulphide.
—	Water at 15·5° C. saturated with chlorine.
—	Pure liquid bromine.
—	Water at 15·5° C. saturated with bromine.
—	Hydrogen peroxide, 20 volume solution.
	,, ,, 10 ,, ,,
KHO	280 grms. dissolved and diluted to 1 litre.
,,	56 ,, ,, ,,
NaHO	200 ,, ,, ,,
,,	40 ,, ,, ,,
—	Ammonium hydroxide sp. gr. 0·880 (liquor ammonia).
—	Ammonium hydroxide diluted to sp. gr. 0·9643 at 15·5°.
—	200 cc. of 5 N ammonium hydroxide diluted to 1 litre.
$BaH_2O_2,8Aq$	52·5 grms. dissolved and diluted to 1 litre.
—	Water at 15·5° C. saturated with calcium hydroxide.
—	Saturate 600 c.c. of 5N ammonium hydroxide with H_2S in a corked flask, and then add 400 c.c. of 5N ammonium hydroxide.
—	200 c.c. of 5N ammonium sulphide diluted to 1 litre.

Name of Reagent.	Symbol.	Molecular weight.	Equivalent weight.	Equivalent System.	
				Grms. per litre.	Strength.
Sodium Sulphide	Na_2S	78	39	—	5N
,,	,,	,,	,,	39	$\dfrac{N}{}$
Potassium Cyanide	KCy	65	65	65	N
Potassium Sulphate	K_2SO_4	174	87	87	N
Potassium Iodide	KI	166	166	166	N
,,	,,	,,	,,	—	$\dfrac{N}{5}$
Potassium Chromate	K_2CrO_4	194·5	97·25	97·25	N
Potassium Metantimoniate	$KSbO_3$	209	209	3·07	$\dfrac{N}{68}$
Potassium Ferrocyanide	K_4FeCy_6	368	92	92	N
Potassium Ferricyanide	$K_6Fe_2Cy_{12}$	658	109·7	109·7	N
Potassium Sulphocyanate	KCyS	97	97	97	N
Sodium Carbonate	Na_2CO_3	106	53	—	3N
,,	,,	,,	,,	53	N
Hydrogen Disodium Phosphate	HNa_2PO_4	142	47·3	47·3	$\dfrac{2N}{3}$ or N
Sodium Acetate	$NaC_2H_3O_2$	82	82	—	4N
Sodium Sulphite	Na_2SO_3	126	63	—	2N –
Sodium Thiosulphate	$Na_2S_2O_3$	158	79	79	$\dfrac{N}{2}$ or N
Sodium Hypochlorite	NaClO	74·5	74·5	—	—
Ammonium Acetate	$NH_4C_2H_3O_2$	77	77	—	5N
,,	,,	,,	,,	77	N
Ammonium Oxalate	$(NH_4)_2C_2O_4$	124	62	37·2	$\dfrac{3N}{5}$
Hydrogen Di-ammonium Phosphate	$H(NH_4)_2PO_4$	32	44	44	$\dfrac{2N}{3}$ or N
Ammonium Carbonate	$(NH_4)_2CO_3$	96	48	—	5N
,,	,,	,,	,,	48	N
Hydrogen Ammonium Carbonate	$H(NH_4)CO_3$	79	39·5	—	$\dfrac{3N}{2}$ or 3N
Ammonium Chloride	NH_4Cl	53·5	53·5	—	5N
,,	,,	,,	,,	53·5	N
Ammonium Sulphate	$(NH_4)_2SO_4$	132	66	66	N
Barium Chloride	$BaCl_2$	208	104	104	N
Barium Nitrate	BaN_2O_6	261	130·5	65·25	$\dfrac{N}{2}$
Barium Carbonate	$BaCO_3$	197	98·5	—	2N
Strontium Sulphate	$SrSO_4$	183·5	91·75	0·153	$\dfrac{N}{600}$
Calcium Chloride	$CaCl_2$	111	55·5	55·5	N

Symbol of Substance taken.	Method of Preparing Reagent.
—	Dissolve 200 grms. of sodium hydrate in 800 c.c. water, saturate one-half with H_2S, then add the other half and dilute to 1 litre.
	200 c.c. of 5N sodium sulphide diluted to 1 litre.
KCy	65 grms. crystals dissolved and diluted to 1 litre.
K_2SO_4	87 grms. dissolved and diluted to 1 litre.
KI	166 ,, ,, ,,
,,	33·2 ,, ,, ,,
K_2CrO_4	97·25 ,, ,, ,,
$K_2Sb_2O_6,7Aq$	Saturated solution at 15·5° C.
$K_4FeCy_6,3Aq$	105·5 grms. dissolved and diluted to 1 litre.
$K_6Fe_2Cy_{12}$	109·7 ,, ,, ,,
KCyS	97 ,, ,, ,,
$Na_2CO_3,10Aq$	429 ,, ,, ,,
,,	143 ,, ,, ,,
$HNa_2PO_4,12Aq$	119·3 ,, ,, ,,
$NaC_2H_3O_2,3Aq$	544 ,, ,, ,,
$Na_2SO_3,7Aq$	252 ,, ,, ,,
$Na_2S_2O_3,5Aq$	124 ,, ,, ,,
—	294 c.c. of 17N acetic acid, neutralised with strong ammonium hydroxide and diluted to 1 litre.
—	200 c.c. of 5N ammonium acetate diluted to 1 litre.
$C_2O_4(NH_4)_2$	42·6 grms. dissolved and diluted to 1 litre.
$H(NH_4)_2PO_4$	44 ,, ,, ,,
—	196·7 grms. of ammonium sesquicarbonate dissolved in 333·3 c.c. of 5N ammonium hydroxide and diluted to 1 litre.
—	200 c.c. of 5N ammonium carbonate solution diluted to 1 litre.
—	A saturated solution made by passing excess of carbon dioxide into 3N ammonium hydroxide.
NH_4Cl	267·5 grms. dissolved and diluted to 1 litre.
,,	53·5 ,, ,, ,,
$(NH_4)_2SO_4$	66 ,, ,, ,,
$BaCl_2,2Aq$	122 ,, ,, ,,
BaN_2O_6	65·25 ,, ,, ,,
$BaCO_3$	197 grms., freshly precipitated, suspended in water, and diluted to 1 litre.
$SrSO_4$	Water at 15·5° C. saturated with precipitated strontium sulphate.
$CaCl_2,6Aq$	109·5 grms. dissolved and diluted to 1 litre.

Name of Reagent.	Symbol.	Molecular weight.	Equivalent weight	Equivalent System.	
				Grms. per litre.	Strength.
Calcium Sulphate	$CaSO_4$	136	68	2·27.	$\frac{N}{30}$
Magnesium Chloride	$MgCl_2$	95	47·5	47·5	$\frac{N}{1}$
Magnesium Sulphate	$MgSO_4$	120	60	60	N
Ferrous Sulphate	$FeSO_4$	152	76	76	N
Ferric Chloride	Fe_2Cl_6	325	54·17	54·17	N
Plumbic Acetate	$PbC_4H_6O_4$	326	162·5	162·5	N
Plumbic Nitrate	PbN_2O_6	331	165·5	165·5	N
Silver Nitrate	$AgNO_3$	170	170	170	N
,,	,,	,,	,,	—	$\frac{N}{5}$
Silver Sulphate	Ag_2SO_4	312	156	7·8	$\frac{N}{20}$
Mercurous Nitrate	$Hg_2N_2O_6$	524	262	5·24 +	$\frac{N}{5} +$
Mercuric Chloride	$HgCl_2$	271	135·5	54·2	$\frac{2N}{5}$
Cupric Sulphate	$CuSO_4$	159·5	79·75	79·75	N
Cupric Chloride	$CuCl_2$	134·5	67·25	67·25	N
Stannous Chloride	$SnCl_2$	189	94·5	94·5 +	N +
Auric Chloride	$AuCl_3$	303·1	101	20·2	$\frac{N}{5}$
Platinic Chloride	$PtCl_4$	339 1	84·8	84·8	N
Magnesia Mixture (for Phosphoric Acid).	—	—	—	—	N

Symbol of Substance taken.	Method of Preparing Reagent.
CaSO$_4$,2Aq	Water at 15·5° C. saturated with precipitated calcium sulphate.
MgCl$_2$,6Aq	101·5 grms. dissolved and diluted to 1 litre.
MgSO$_4$,7Aq	123 ,, ,, ,,
FeSO$_4$,7Aq	139 ,, ,, ,,
—	8·67 grms. of iron, as Fe$_2$H$_6$O$_6$, dissolved in 200 c.c. of 5N hydrochloric acid and diluted to 1 litre.
PbC$_4$H$_6$O$_4$,3Aq	189·5 grms. dissolved and diluted to 1 litre.
PbN$_2$O$_6$	165·5 ,, ,, ,,
AgNO$_3$	170 ,, ,, ,,
,,	34 ,, ,, ,,
Ag$_2$SO$_4$	Water at 15·5° C. saturated with freshly precipitated argentic sulphate.
Hg$_2$N$_2$O$_6$,2Aq	56 grms. dissolved in 40 c.c. 5N nitric acid and diluted to 1 litre, a little mercury being placed in bottle.
HgCl$_2$	54·2 grms. dissolved and diluted to 1 litre.
CuSO$_4$,5Aq	124·75 ,, ,, ,,
CuCl$_2$,2Aq	85·25 ,, ,, ,,
SnCl$_2$,2Aq	112·5 grms. dissolved in 200 c.c. of 5N hydrochloric acid and diluted to 1 litre, a little tin being placed in bottle.
—	13·1 grms. of metallic gold, converted into auric chloride, dissolved, and diluted to 1 litre.
—	49·3 grms. of metallic platinum, converted into platinic chloride, dissolved, and diluted to 1 litre.
—	Dissolve 68 grms. MgCl$_2$,6Aq in about 500 c.c. of water, add 165 grms. NH$_4$Cl, then 300 c.c. of 5N ammonium hydroxide, and dilute to 1 litre.

COMPARISON OF METRIC AND BRITISH UNITS.

Metric to British.   *British to Metric.*

WEIGHT.

Metric to British		British to Metric	
1 gram	= 15·432 grains	1 grain	= 0·064799 grams
1 gram	= 0 035274 oz.	1 oz.	= 28·349 grams
1 kg.	= 2·2046 lbs.	1 lb.	= 0·45359 kg.
1 kg.	= 0·019684 cwts.	1 cwt.	= 50·802 kg.
1 Tonne	= 0·98421 tons	1 ton	= 1·0160 Tonne

LENGTH.

1 Meter	= 1·0936 yards.	1 yard	= 0·91438 Meters
1 Meter	= 3·2809 feet.	1 foot	= 0 30479 Meters
1 cm.	= 0·39371 in.	1 inch	= 2·5400 cm.

AREA.

1 sq. cm.	= 0·15501 sq. in.	1 sq. in.	= 6·4514 sq. cm.
1 sq. M.	= 10·764 sq. ft.	1 sq. ft.	= 0·092900 sq. M.

VOLUME.

1 c.c.	= 0·061027 c. in.	1 c. in.	= 16·386 c.c.
1 c.M.	= 35·317 c. ft.	1 c. ft.	= 0·028315 c. M.
1 litre	= 1·7608 pints	1 pint	= 0·56793 litres

PRESSURE.

1 atmos.	= 0·00656 tons sq. in.	1 ton sq. in. = 152 atmos.
1 atmos.	= 14·7 lbs. sq. in.	1 lb. sq. in. = 0·6080 atmos.
1 kg. sq. cm.	= 0·968 atmos.	1 atmos. = 1·03 kg. sq. cm.
1 kg. sq. cm.	= 14·223 lbs. sq. in.	1 lb. sq. in. = 0·070309 kg. sq. cm.
1 kg. sq. cm.	= 0·0063493 tons sq. in.	1 ton sq. in. = 157·49 kg. sq. cm.

ENERGY.

1 M. Tonne	= 3·2291 foot tons.	1 foot ton	= 0·30969 M. Tonne
1 M. kg.	= 7·2331 foot lbs.	1 foot lbs.	= 0·13825 M. kg.

ADDENDUM

HYDROGEN DIOXIDE or **PEROXIDE,** H_2O_2.—This substance is formed when some metallic peroxides, as BaO_2, PbO_2 (see p. 20) are treated with acids. Thus $BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$. The conditions are that the acids be dilute and temperature low, otherwise the reaction becomes $2BaO_2 + 2H_2SO_4 = 2H_2O + 2BaSO_4 + O_2$. After separation of the insoluble barium sulphate the hydrogen dioxide can be concentrated by freezing the weak aqueous solution. Much water separates as ice, and the dioxide can then be further concentrated by evaporating under reduced pressure and over sulphuric acid.

When pure it forms a colourless and slightly viscous liquid of relative weight 1·46. It is easily decomposed on contact with many substances, and on heating, and is always employed in a more or less dilute aqueous solution. It is industrially employed for bleaching hair, feathers, silk, &c. On contact with metallic peroxides, as MnO_2, or alkali permanganate, it evolves oxygen. The reaction with the latter is $K_2Mn_2O_8 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$ (characteristic). Potassium iodide and starch paste to which ferrous sulphate has been added becomes coloured blue by H_2O_2.

A very dilute acid solution of potassium bichromate forms a deep blue coloured compound with traces of H_2O_2. The blue substance dissolves in ether. A solution of titanium sulphate forms with H_2O_2 an orange-red coloration.

It is possible that in a number of oxidation processes H_2O_2 is formed in small amount, and then conveys some oxygen to the substance undergoing oxidation, a further quantity of H_2O_2 being formed, and so on.

A small quantity is formed sometimes in the electrolysis of acidified water, and some can also be found in the products of combustion of hydrogen, especially when this gas is burnt at a very small jet.

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